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The Infra-red Absorption Spectra of Alkali Hydroxides. G. R. GRANTHAM 339
An Absolute Scale of X-Ray Wave Lengths. OSWALD B. OVERN 350
Thermal Conductivity of Some Wearing Materials. EMILY S. ROOD 356
Vapor Pressure of Metallic Calcium. NORMAN R. PILLING 362
Light Emission from a Moving Source in Connection with the Relativity Theory. N. RASHEVSKY 369
Note on the Plane Wave in an Isotropic Dielectric. SATYENDRA RAY 377
Note on Radiation Pressure. R. N. GHOSH AND N. K. SUR 380
The Ionization Potential of Selenium Vapor. A. D. UDDEN 385
On Talbot's Bands and the Theory of the Lummer-Gehrcke Interferometer. NIHAL KARAN SETHI 389
The Reflection of X-Rays by Crystals. H. A. WILSON 396
The Effect of the Age and the Concentration of a Solution of Rhodamine-B upon the Photoelectric Current Developed. RUTH YEATON JENKINS 402
Temperature Effect in Barium and Strontium Photo-Electric Cells. THEODORE W. CASE 413

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Second Series *November, 1921* *Vol. XVIII, No. 5*

THE

PHYSICAL REVIEW.

THE INFRA-RED ABSORPTION SPECTRA OF ALKALI HYDROXIDES.

By G. E. Grantham.

Synopsis.

Infra-red Absorption of Aqueous Solutions of Alkali Hydroxides, 1–3 μ.—The absorption of various concentrations of solutions of *NaOH, KOH and LiOH* and of one solution each of *NH_4OH and CsOH* was determined with reference to that of water, using two like cells with quartz windows, and a suitable spectrometer with thermopile and sensitive galvanometer. All curves show a broad, intense absorption band with a maximum at about 2.29 μ except in the case of the NH_4OH solution for which the maximum is at 2.20 μ. This agreement suggests that the band is due to dissociated hydroxide ions; yet in the case of other hydroxide solutions previous observers have not obtained an absorption band at this place. The absorption was found to be proportional to the concentration but not to vary systematically with the atomic weight of the base of the hydroxide. In the case of KOH the relative absorption results were checked by actual absorption measurements.

The Coefficient of Absorption of Water, 1.3 to 2.0 μ was measured by comparing the transmissions of cells of different thicknesses. Maximum absorption was observed at 1.48 and 1.98 μ. *The effect of dissolving an alkali hydroxide* is to decrease the absorption of the water in the band at 1.48 μ by an amount proportional to the concentration of the solution and to the atomic weight of the base.

Introduction.

An investigation of the ultra-violet and visible absorption spectra of aqueous alkaline solutions of phenoltetrachlorophthalein by Howe and Gibson[1] showed absorption bands at frequency numbers 3590, 2760 and 1740. These bands are approximately harmonic and it seemed desirable to search for the next band of the harmonic series which should have a frequency number of about 900, or a wave-length of approximately 1.1 μ. This search proved fruitless, but in the region 1.7 μ it was found that a given thickness of a ten gram molecule per liter aqueous solution of NaOH transmitted less energy than did an equal thickness of phenol-

[1] Phys. Rev., S. II., Vol. X, 1917.

tetrachlorophthalein in a ten gram molecule per liter aqueous solution of NaOH. Further trial showed that NaOH has a strong absorption in this region and that the result just described was due to a di-sodium salt being formed in the cell containing the phenoltetrachlorophthalein, which formation used up n gram molecules per liter of the NaOH, thus, in effect, making this cell contain a less thickness of NaOH. This suggested a study of the absorption spectra of alkaline hydroxides in the region 1.0 μ to 3.0 μ. The measurements were made by means of a spectrometer in conjunction with a thermocouple and galvanometer.

METHOD.

Owing to the strong absorption of aqueous solutions in this region, a differential method was adopted. The deflection d_1 was taken when the radiation was passing through a given thickness of water, and an instant later the deflection d_2 was taken when the radiation was passing through an equal thickness of the aqueous hydroxide solution. This made it possible to have the two galvanometer deflections of the same order of magnitude, and to work with the galvanometer in a more sensitive condition. The values d_1 and d_2 were taken at least three times for each wave-length, or until consistent results were obtained. Readings were taken at each 0.1 μ except in the region of a peak on the transmission curve where they were made more frequently. A sample of the data obtained is shown in Table I. These values were selected at random from a complete set of data for KOH and represent about one third of the values taken for one curve. The per cent. relative transmission was calculated from the equation: Transmission $= (d_1/d_2) \times 100$.

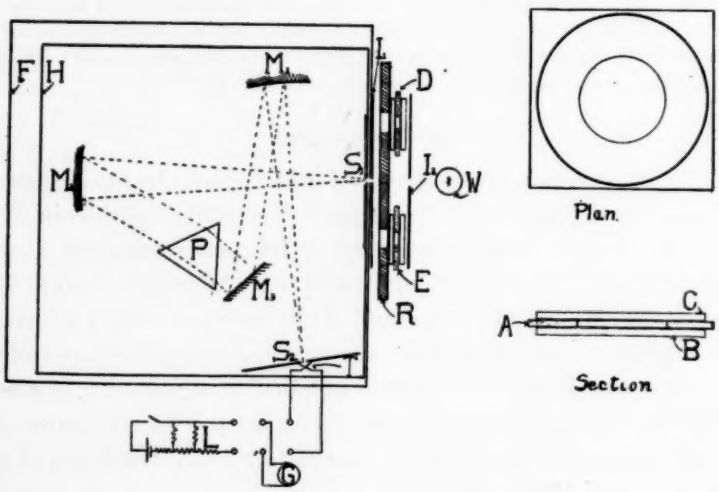

Fig. 1.

APPARATUS.

The apparatus used is shown in Fig. 1. The galvanometer and spectrometer have been quite fully described by the writer in a previous article.[1] The spectrometer was of the Hilger constant deviation type equipped with a rock salt prism P and a Coblentz[2] bismuth-silver thermopile T. When adjusted the instrument gave the following values for the three absorption bands of water and the carbon dioxide emission band respectively; 1.48 μ, 1.98 μ, 3.0 μ and 4.36 μ. These points were checked from time to time during this work. The spectrometer was covered by a glass case H, which was in turn covered by a sheet iron case F. The inside walls of H were covered with black cloth to prevent reflection. A 2.5 watt electric lamp was kept burning continuously immediately under the spectrometer to prevent dew formation, and P_2O_5 was used to keep the air surrounding the prism dry. During the experiments the slits S_1 and S_2 were 0.25 mm. wide.

A Coblentz[3] astatic galvanometer G was used. The sensibility of the galvanometer was adjusted to approximately 3.3×10^{-11} ampere per mm. at three meters distance. The sensibility was measured by means of the testing box L, which was furnished with the galvanometer. No deflection greater than 35 cm. was used.

The source of radiation W was a 400-watt nitrogen filled lamp which was supplied with current from a 120-volt storage battery.

The cells which contained the solutions were made as follows: A piece of plane glass was ground until its thickness was uniform and was then cut into two parts, each of which was four centimeters square. Through the center of each of these parts a hole 2 cm. in diameter was ground, making two glass washers. To assemble a cell one of these washers A was placed upon a quartz plate B, the small volume formed by the hole and the quartz plate filled with the solution, and another quartz plate C placed over the glass washer. These three parts were then clamped together and placed upon the slide R at D. The other cell was made similarly, using the other glass washer filled with water and mounted on the slide at E. The four quartz plates used were of equal thickness. Sheet iron screens I_1 and I_2, with holes 1.5 cm. in diameter, permitted no radiation to enter the slit S_1, except that which had come through the water, or solution in a cell. The pairs of washers used for different regions in the spectrum were 3.77 mm., 1.29 mm., 0.84 mm. and 0.15 mm. thick. Unless otherwise stated in this paper the thickness of the cell used was 0.84 mm.

[1] PHYS. REV., S. II., Vol. XVI., 1920.

[2] Bulletin of the Bureau of Standards, Vol. 9, 1912.

[3] Bulletin of the Bureau of Standards, Vol. 4, 1908. Bulletin of the Bureau of Standards, Vol. 9, 1912. Scientific Papers of the Bureau of Standards, No. 282.

TABLE I.

Ten gram molecule per liter aqueous solution of KOH.
Thickness 0.84 cm.

μ	d_1 mm.	d_2 mm.	Transmission, Per Cent.	Average, Per Cent.
1.0	85	85	100	100
	85	85		
	85	85		
1.3	199	201	101	100.3
	195	195		
	202	202		
1.4	135	165	122.3	121.6
	135	163	121	
	135	164	121.5	
1.5	81	109	135	135.3
	80	109	136	
	81	109	135	
1.7	212	103	48.6	48.9
	210	103	49.0	
	210	103	49.0	
2.0	141	50	35.5	35.1
	139	48	34.6	
	139	49	35.2	
2.1	137	32	23.3	23.3
	132	32	24.3	
	131	31	23.7	
2.2	168	25	14.9	15.5
	165	26	15.8	
	165	26	15.8	
2.3	252	38	15.1	14.9
	252	37	14.7	
	250	37	14.8	
2.5	59	21	35.6	35.6
	59	21		
	59	21		
2.7	25	18	72	71.7
	24	17	71	
	22	16	72.7	
	24	17	71	
2.9	18	15	83.4	83.4
	18	15		
	18	15		

RESULTS.

The absorption for different concentrations of NaOH, LiOH and KOH was observed as described above. The absorption for a 0.25 gram molecule per liter aqueous solution of CsOH and for an approximately 15 gram molecule per liter solution of NH_4OH was also observed. The results of these investigations are shown graphically in Figs. 2–7. Figs.

2, 3 and 4 show the absorption curves for different concentrations of the aqueous solutions of the alkali hydroxides. These curves are similar, each showing evidence of strong absorption in the region between 1.5 μ and 2.6 μ with a maximum of absorption at about 2.29 μ. There is

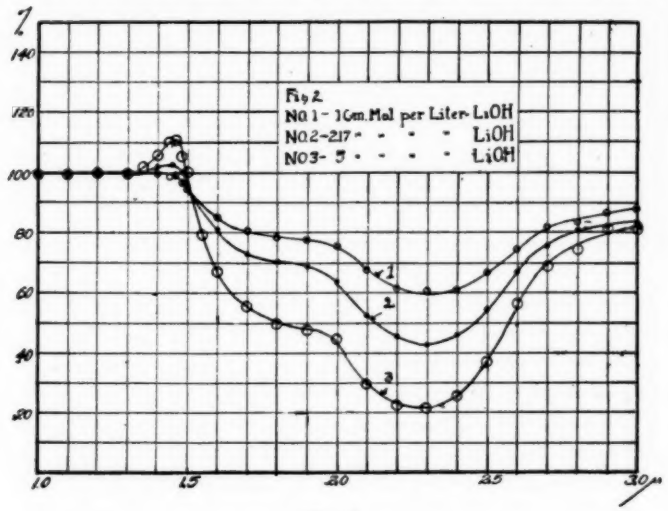

Fig. 2.

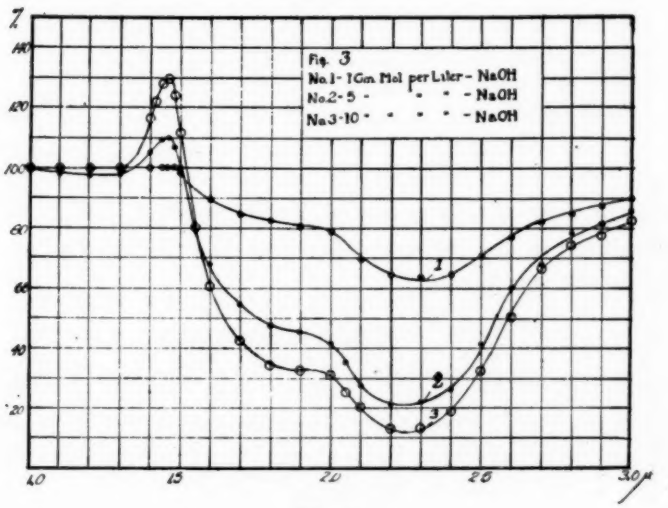

Fig. 3.

practically no difference in the absorption of a given thickness of water such as was used in this investigation, and that of an equal thickness of solution of X-OH in the region from 1.0 μ to 1.3 μ. From 1.3 μ to 1.55 μ the absorption of a given thickness of water is much greater than

the absorption of the same thickness of a solution of X-OH. This range (1.3 μ to 1.55 μ) includes a sharp absorption band due to water at 1.49 μ. It also includes a region of weak absorption for X-OH. There is in the X-OH cell a less number of water molecules than in the water cell due to the replacement of water molecules by the X-OH molecules. If the X-OH absorption was weak in this region, a transmission value higher than 100 per cent. would be expected by this method. This explanation, however, does not account for the high values of transmission obtained. The density of a ten gram molecule per liter aqueous solution of KOH was found from chemical tables to be 1.414 grams per c.c. In this

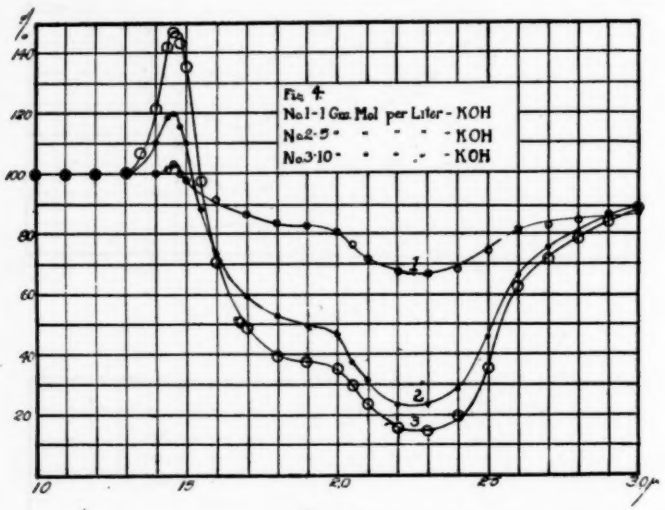

Fig. 4.

solution there were 561.00 grams of KOH per liter. The thickness of the solution used in the cell was 0.84 mm. The actual thickness of the water in this cell was then

$$\frac{1414 - 561}{1000} \times 0.84 = 0.716 \text{ mm.}$$

If the coefficient of absorption of water was known, the per cent. of transmission for equal thicknesses of solution and of water, assuming that the KOH had no effect either as an absorbing agent itself or in modifying that of the water, could be calculated. The coefficient of absorption of water was measured in the following manner: Two cells of different thickness, filled with water, were mounted on the slide and the energy transmitted by each, for wave-lengths in the region 1.3 μ to 2.0 μ, was measured. The values of the coefficient of absorption were then calculated from the relation:

$$\beta = \frac{1}{c(t_2 - t_1)} \log I_1/I_2$$

where c is the concentration, taken as unity, and I_1 and I_2 the energy transmitted at a given wave-length through cells of thickness t_1 and t_2 respectively. The different values of β were obtained using cells of thickness 0.84 mm. and 1.183 mm. The measurements were then repeated using cells of thickness 0.84 mm. and 1.290 mm. and the mean value for β used. Using these values of β and 0.84 mm. and 0.716 mm. for t_2 and t_1 respectively, the values of I_1/I_2 were calculated for this region of the spectrum. These results are shown graphically in Fig. 5, curve No. 2. Curve No. 1 is the observed per cent. transmission curve for a ten gram molecule per liter aqueous solution of KOH, while No. 2 shows the corresponding values for the same solution calculated in the manner just described. Curve No. 1 shows a maximum ordinate at 1.46 μ of

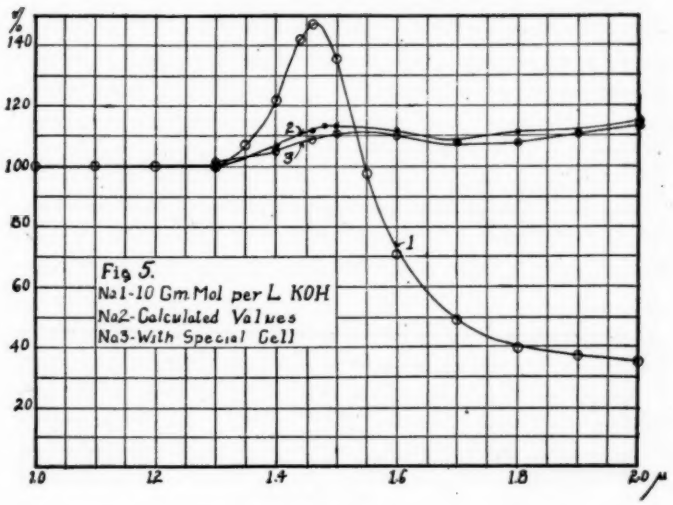

Fig. 5.

value 147 per cent., while, if this increase in transmission was due to the different thickness of water, the maximum value of the ordinate should be 112 per cent. This indicates that the presence of KOH has an effect upon the absorption of water, which effect is to make the transmission greater. A similar calculation with similar results was made for NaOH. The heights of these peaks as seen from Figs. 2, 3 and 4 are roughly proportional to the concentration for a given hydroxide, and to the atomic weight of the base for different hydroxides. The peak of the transmission band is at 1.46 μ in each case, while the maximum absorption of water in this region is shown by Fig. 7, curve No. 2 to be at 1.49 μ. This apparent shift of 0.03 μ toward the shorter wave-lengths is explained by the overlapping of the X-OH absorption band on the transmission band. If it

were not for this overlapping, the maximum of the transmission bands, shown in Figs. 2, 3 and 4 might coincide with the maximum absorption of water.

In order to check the method just described for testing the replacement of water molecules by KOH the following suggestion was acted upon.

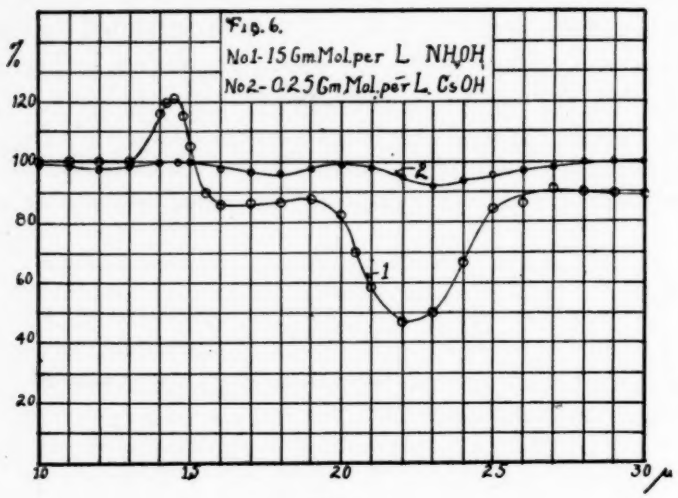

Fig. 6.

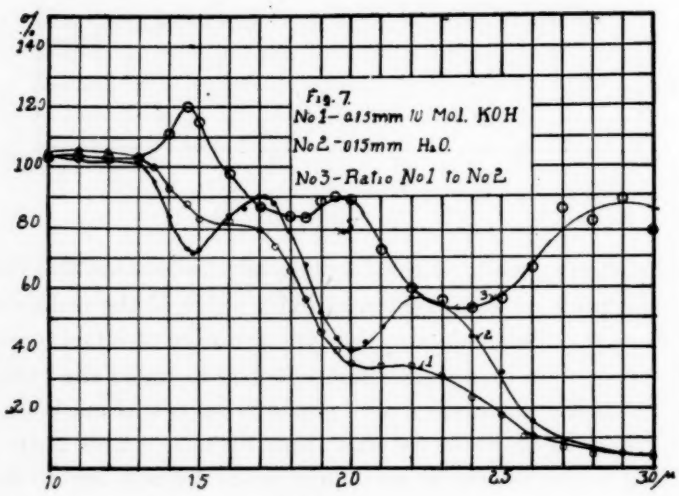

Fig. 7.

By using one cell 0.84 mm. thick and the other of the same thickness as the actual layer of water in a cell 0.84 mm. thick, filled with a ten gram molecule per liter aqueous solution of KOH, namely, 0.716 mm., the per cent. transmission could be obtained directly. In an attempt to

grind a glass washer of this thickness and keep it uniform the grinding was carried too far, and a cell 0.705 mm. thick was obtained. The results of the use of the cells 0.84 mm. and 0.705 mm. thick are shown in Fig. 5, curve No. 3. These results check, as well as could be expected, with those calculated above.

On the transmission curves shown in Figs. 2, 3 and 4 there is a hump at wave-length 2.0 μ. This is also the location of a strong absorption band of water, as shown by Fig. 7, curve No. 2. This hump may be due to the same effect as the peak at 1.46 μ. It lies, however, in the region of strong absorption of X-OH, and for this reason a similar conclusion cannot be drawn from calculations. Owing to this increase in transmission at 2.0 μ the minimum of the transmission curves, which lies at 2.29 μ, may be shifted toward the longer wave-lengths, and it is therefore probable that the maximum of absorption of the X-OH solutions is at a slightly shorter wave-length than 2.29 μ. Since the absorption curves for the hydroxides of the alkali metals tested are similar, it is evident that the absorption is due to the OH radical. This conclusion is further substantiated by the fact that, at a given wave-length, the magnitude of the absorption for the same strength of different solutions shows no systematic variation with atomic weight of the base. The position of the minimum at 2.29 μ does not shift with the change of atomic weight of the base.

Fig. 7, curve No. 1 shows the actual transmission of a 0.15 mm. thickness of a ten gram molecule per liter aqueous solution of KOH, and No. 2 the transmission of the same thickness of water. Curve No. 3 shows the result of plotting the ratio of the ordinates of curves No. 1 and No. 2. This curve is similar to those of Figs. 2, 3 and 4. The relatively strong transmission of the empty cell made it necessary to use the galvanometer at low sensibility, and consequently the accuracy of measurement was not as great for the curves of this figure as for those of Figs. 2, 3 and 4. A study of Fig. 7, curves No. 1 and No. 2 shows the region of the strongest absorption of the KOH to be from 1.8 μ to 2.5 μ.

Fig. 6, curve No. 1 shows the transmission of an approximately 15 gram molecule per liter solution of NH_4OH. In this curve there is a shift of the minimum to 2.2 μ, and the hump in the curve at 2.0 μ is much more pronounced than in the case of the hydroxides of the alkali metals. Curve No. 2 shows the transmission of a 0.25 gram molecule per liter aqueous solution of CsOH. The solution was very weak, due to lack of chemicals. No attempt was made to study the absorption of RbOH for the same reason.

Ransohoff[1] has studied the effect of the OH group on absorption using six alcohols. He found bands at 1.71 μ and 3.0 μ, neither of which falls in the region of the strong absorption found in this investigation. Coblentz[2] has studied the absorption of $Mg(OH)_2$ and other hydroxides of elements not in the alkali metal group, and his results show no absorption in the region 2.29 μ. This would indicate that the band is present only in strongly alkaline hydroxides.

From Fig. 7, curve No. 1 it is seen that the effect of the absorption band of water at 1.49 μ is much less marked in the absorption curve of the KOH solution, than the effect of the absorption band of the water at 2.0 μ. It is probable that this absorption band of water would disappear, if the concentration of the X-OH were sufficiently high. Coblentz[3] has shown that the strong absorption band of solid iodine at 7.3 μ disappears when the iodine is placed in solution. This is caused by the action of the solvent upon the absorption of the solute, while the effect here described is the effect of the solute upon the absorption of the solvent.

In papers by Guy, Schaeffer and Jones[4] and by Schaeffer, Paulus and Jones,[5] curves appear that show similar effects upon the absorption bands of water at 1.0 μ and 1.24 μ, when various metallic salts are dissolved in water. The maximum absorption of the solutions does not, in many of the cases shown, occur at the same wave-length as that of the water. The ratio of transmission of solution to the transmission of a layer of water, equal in thickness to that contained in the solution at the positions of maximum absorption for each, is as large as 1.21 for 2.14 normal solution of $MgSO_4$ and 1.16 for 1.02 normal solution of $Al_2(SO_4)_2$.

Livens[6] in a theoretical paper discusses the effect of solute upon the absorption of a solvent, and points out that a shift in the position of the absorption bands should accompany a change in the intensity of the maximum absorption.

Conclusions.

The following conclusions may be drawn from these investigations:

1. There is a broad, intense absorption band in the spectra of the alkaline hydroxides in the region 1.5 μ to 2.7 μ.

2. The absorption is roughly proportional to the concentration of the solution for a given hydroxide.

3. There is no systematic variation of the absorption with the atomic weight of the base.

[1] Berlin Inaugural Dissertation, January, 1896.

[2] Scientific Papers of the Bureau of Standards, No. 45, 1907.

[3] PHYS. REV., XVI., I., 1903.

[4] Phys. Zeits., Vol. 14, p. 278, 1913; Amer. Chem. Jour., 49, p. 265, 1913.

[5] Phys. Zeits., Vol. 15, p. 447, 1914; Chem. News, 110, p. 223, 1914.

[6] Phys. Zeits., Vol. 14, p. 660, 1913.

4. The absorption is probably due to the dissociated hydroxide ions, as the absorption is not present in the alcohols, or other compounds which have the OH radical.

5. The presence of an alkaline hydroxide in solution with water decreases the actual absorption of the water present. This effect of the solute upon the absorption of the solvent increases with the concentration. This shows evidence of a change of the physical properties of the water molecule, when it becomes the solvent.

This investigation was carried on in the Physics Laboratory of Cornell University. The writer wishes to thank Professor R. C. Gibbs, under whose direction this work was done, for his interest and advice throughout this investigation and the writing of this report. He wishes also to thank Professor W. R. Orndorff of the Chemistry Department for advice regarding the chemistry involved, Dr. S. D. Jackson and Mr. R. T. K. Cornwell of the Chemistry Department for making up the standard solutions and his wife, Margaret Grantham, for assistance in taking the data and computing the results.

U. S. Naval Academy,
Annapolis, Maryland.

AN ABSOLUTE SCALE OF X-RAY WAVE-LENGTHS.

BY OSWALD B. OVERN.

SYNOPSIS.

Absolute Scale of X-Ray Wave-Lengths Based on Discontinuities Due to Analyzing Crystal.—In a previous study of the continuous spectrum from a tungsten target, an absorption line was observed at 0.7928 × 10^{-8} cm. This result has been confirmed with a molybdenum target, light lines being obtained at 0.7926 and 0.4288 × 10^{-8} cm. To get these lines with a rock salt crystal a thickness of less than 10^{-2} cm. was necessary. *In explanation of the discontinuities* it was suggested by A. W. Hull that when any wave-length is reflected by two sets of crystal planes, the energy is divided so that the intensity of the part which reaches the photographic plate is less than for wave-lengths on either side. For each pair of sets of planes the critical wave-length is fixed by the geometry of the crystal alone. Taking the grating constant for rock salt as 2.814 × 10^{-8} cm., the wave-lengths computed for the planes 100/210 and 100/310 are 0.7959 and 0.4316 × 10^{-8} cm. respectively. Using these as *reference points*, the center of the scale of wave-lengths may be accurately determined and a scale of wave-lengths may be established independent of everything except the grating constant.

Bromine and Silver X-Ray Absorption Limits come near the above reference points and were thus *accurately located* at 0.9186 and 0.4842 × 10^{-8} cm., in close agreement with the values given by Blake and Duane.

K Series of Molybdenum.—The wave-lengths of five lines were determined by reference to 0.7959 × 10^{-8} cm. more accurately than in previous measurements.

IN a former paper[1] the author has described some work done at the University of Iowa on the tungsten spectrum and has shown a photograph of a light line which appeared very clearly in the region of the bromine absorption band at a wave-length of .7928 × 10^{-8} cm.

Later de Broglie[2] has published a paper in which he states that he has verified all the other results of the author on the tungsten spectrum but that he has not found this line. Since de Broglie's work has evidently been done with great care, this line might appear to have been a false effect.

The experiment has therefore been tried again with a

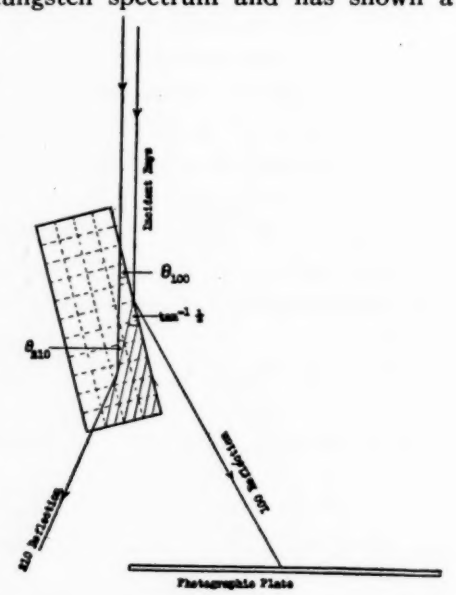

Fig. 1.

[1] PHYS. REV., N. S., Vol. XVI., Dec., 1920, p. 526.

[2] Phil. Mag., Nov., 1919.

molybdenum tube at the University of Chicago. A light line has again been found to appear unmistakably at a wave-length of .7926 × 10^{-8} cm. as compared with the wave-length .7928 × 10^{-8} cm. previously found.

Apparatus and Method.

The source of the rays was a Coolidge tube with a molybdenum target excited by means of a transformer, the tube rectifying its own current. The continuous spectrum was produced by a thin crystal of rock salt rotated slowly by clockwork. The exposure was twenty hours per degree of rotation with a constant input of 150 watts. The distance from plate to crystal axis was kept in the neighborhood of 30 cm. and the slit was .030 cm. in width. The wave-lengths were measured by Dershem's method[1] thus eliminating the necessity of correcting for depth of penetration into the crystal. The spectrometer although differing widely in detail, was constructed on the same principle as that used by Dershem and will therefore require no description here.

Results.

It was found that these lines could not be produced clearly using a thick crystal. Indeed, one crystal which failed to produce an effect when it had a thickness of .013 cm. gave a clear photograph of the line .7926 × 10^{-8} cm. when ground down to a thickness of .006 cm. It would seem that the crystal must have a thickness less than about .01 cm. in order to produce a clear image of this line. The crystal which produced the best photograph had an average thickness of .0059 cm. Under conditions as outlined above, this line will appear very readily.

The line of wave-length .4288 × 10^{-8} appears very feebly as would be expected from the fact that there are fewer atoms in the planes reflecting the radiation away from the plate at this point and it is therefore very difficult to measure it accurately. It has been found on only one plate since lack of time prevented my finding it a second time. For this reason the measurement is probably somewhat uncertain.

Theory.

I am indebted to Dr. A. W. Hull for suggesting the following very interesting interpretation of the meaning of these light lines.

The depth of penetration of the reflected rays into the crystal and hence the intensity of the photograph is limited by absorption. For the small angles under consideration a large part of this absorption is scattering. But the scattering due to any set of planes is small except when it is at the angle of perfect reflection.

[1] Phys. Rev., N. S., Vol. XI., June, 1918, p. 461.

Let us suppose, for example, that the homogeneous spectrum is being reflected to the photographic plate by a set of planes A. As the crystal is rotated it may come to the angle of perfect reflection for another set of planes B with the result that the crystal suddenly becomes more opaque to the rays which should be reflected from A; *i.e.*, some of the radiation which we should expect to be reflected by the set A is reflected in another direction by the set B and does not reach the photographic plate. The intensity of the photograph will therefore be diminished at the wave-length where this occurs and a light line will result.

The angle at which this will occur depends upon the relative positions of the two sets of planes. To illustrate, let us suppose that the continuous spectrum is being produced by the 100 planes and that the crystal is rotated until it reaches a position where the same wave-length, λ, is reflected simultaneously by the 100 and 210 planes.

Then

$$\lambda = 2d_{100} \sin \theta_{100} = 2d_{210} \sin \theta_{210},$$

or

$$\sin \theta_{210} = \frac{d_{100}}{d_{210}} \sin \theta_{100}.$$

But since

$$\frac{d_{100}}{d_{210}} = \sqrt{5}.$$

We have

$$\sin \theta_{210} = \sqrt{5} \sin \theta_{100}. \qquad (1)$$

Another relation is evident from Fig. 1, namely,

$$\theta_{100} + \theta_{210} = \tan^{-1} \tfrac{1}{2}. \qquad (2)$$

Equations (1) and (2) fully determine θ_{100} and θ_{210}. Solving, we get,

$$\theta_{100} = 8^\circ\ 7'\ 48'',$$
$$\theta_{210} = 18^\circ\ 26'\ 06''.$$

And

$$\lambda = 2d \sin \theta = .7959 \times 10^{-8} \text{ cm}.$$

Other combinations of atomic planes should produce other lines as indicated in Table I.

TABLE I.

Grating constant for rock salt = $d = 2.814 \times 10^{-8}$ cm.

Planes.	Wave-Lengths in 10^{-8} cm.	Observed Values.	Correction.
100 and 210.....	.7959	.7926 and .7928	+.0033 and +.0031
100 and 310.....	.4316	.4288	+.0028
100 and 320.....	1.103		
100 and 110.....	1.779		

The intensity of these lines would vary in accordance with the relative number of atoms in the planes producing them. The absorption coefficients of the crystals used would also have some effect in changing the relative intensity. However, it seems reasonable to suppose that the first three lines mentioned in the table should be visible with a rock salt crystal.

Several attempts were made to find the first three lines. As shown in the third column, these attempts have met with success in the first two cases only. The line of wave-length 1.103×10^{-8} was obscured on the photographs (if it did exist) by the fact that it is very close to the γ_1 line of tungsten which appeared on all the molybdenum photographs of this region.

An Absolute Scale of X-Ray Wave-Lengths.

The wave-lengths .7959 and .4316, as determined above, depend only upon constants of the crystal and are totally independent of the apparatus. They therefore furnish a method of finding the center correction more accurate than any other yet devised.

Furthermore, any wave-lengths of lines appearing on the same plat in the immediate region of one of these light lines may be corrected bye adding the difference between the calculated and observed values of these light lines as shown in the fourth column. Wave-lengths so found should be more accurate than those found by other methods provided the measurements are accurate. They would be subject to twice the error in the dividing engine used in measuring the plates and to the error in the grating constant but to *no other error*. An *absolute* scale of wave-lengths is thus established.

The Bromine Absorption Band.

The bromine absorption band always appears on photographs with a sharp critical absorption edge and so furnishes a convenient reference line. It lies very close to the line .7959 and hence the above-mentioned correction can be applied to it.

Table II.

Bromine Critical Absorption Wave-Length $\times 10^8$.

	Obs. Value.	Correction.	Corrected Value.	Blake and Duane.[1]
Plate A.....	.9151	+.0033	.9184	.9179
Plates 210, 213.....	.9157	+.0031	.9188	

The average value of the critical absorption wave-length found by this method is seen from Table II. to be .9186 × 10^{-8} cm. which agrees within one tenth of one per cent. with the value found by Blake and Duane.[1]

The Silver Absorption Band.

The silver critical absorption wave-length appears on the same plate as the line .4288 × 10^{-8} and lies near it in the spectrum. Hence it can be determined as follows:

Observed Ag. abs. wave-length	.4814 × 10^{-8} cm.
Correction	+.0028
Corrected value	.4842 × 10^{-8} cm.

Here the corrected value is within two tenths of one per cent. of the value given by Blake and Duane, namely, .4850 × 10^{-8} cm.

The K Series of Molybdenum.

The K series lines of molybdenum all appear on the same plates with the line .7959 × 10^{-8} and can be corrected as follows:

	Plate A.		Plates 210 and 213.		
Designation.	Observed Value.	Corrected Value.	Observed Value.	Corrected Value.	Average Corrected.
Light 210/100	.7926	.7959	.7928	.7959	.7959
Mo α_2	.7099	.7132	.7099	.7130	.7131
Mo α_1	.7055	.7088	.7056	.7087	.7087
Mo β	.6294	.6327	.6291	.6322	.6324
Mo	.6235	.6268	——	——	.6268
Mo γ	.6181	.6214	——	——	.6214

These corrected wave-lengths should be more reliable than any other values heretofore found.

The K Series of Tungsten.

For comparison, one photograph has been made of the second order K series lines of tungsten. Only α_2 and α_1 appeared on the plate. These lines are quite close to the silver absorption edge and so can be calibrated from its wave-length after this has been corrected by means of these light lines. The distance between crystal and plate for this photograph was 48.136 cm. and the center of the scale was found by calling the wave-length of the silver absorption edge .4842 × 10^{-8} as determined above. This gives the correct values at once. The measurements are as follows:

[1] Phys. Rev., N. S., Vol. X., 1917, p. 700.

K Series of Tungsten.

Designation.	Distance from Center.	Wave-Length in 10^{-8} cm.	Siegbahn.	Duane and Patterson.
Ag. Abs.....	8.3760 cm.	.4842		
W K α_2.....	7.3735 cm.	.2136	.21352	.21348
W K α_1.....	7.1863 cm.	.2083	.20885	.20867

The results of Siegbahn[2] and Duane and Patterson[1] are listed for comparison, those of Duane and Patterson being changed slightly to make them conform to the grating constant here used.

The extreme faintness of the line $.4316 \times 10^{-8}$ by which the silver absorption edge is calibrated introduces a certain degree of uncertainty into these results. However, the agreement is as good as could be expected under the circumstances.

More accurate determinations of the wave-lengths of these light lines would seem to be of great importance to the study of x-ray spectroscopy. Further work along these lines is now being done at the Ryerson Physical Laboratory.

In conclusion, the author wishes to express his thanks to Dr. A. W. Hull for his suggestions, to Professor R. A. Millikan for his kindly interest, and to Mr. Erik Andersen for valuable assistance rendered in the experimental work.

THERMAL CONDUCTIVITY OF SOME WEARING MATERIALS.

BY EMILY S. ROOD.

SYNOPSIS.

Thermal Conductivity of Woolen, Cotton, Linen and Silk Materials.—Measurements of the conductivity of samples of knitted and woven materials have been made by the disk method of Lees, corrected for variation of emissivity with temperature. From one to eight or more layers of one of the materials were held between two copper disks with a pressure of 6 gm./cm.², one disk being heated electrically by a coil between it and a third disk, and all three radiating to a constant temperature enclosure. The temperature of the samples was 30 to 40°. The values obtained are greater for dense than for loosely woven or knitted samples, ranging from 76 for unspun silk, 94 to 120 for wool, 101 to 122 for silk, 131 for flannelette, 158 to 167 for linen, to 168 to 184 for cotton, all times 10^{-6}. The results come out greater for several layers than for a few, and greater for moist than for dry samples. When the materials are arranged according to conductivity for equal weight instead of equal thickness, the order depends largely on the looseness of texture, beginning with unspun silk, loosely woven wool and knitted artificial silk, and ending with closely woven silk cotton and linen.

THE common textbooks on heat and the standard physical tables show both a lack of data, and great discrepancies in the results given for the thermal conductivity of materials such as wool, cotton, silk. Poynting and Thomson quote Péclet's value for wool .00012 and for cotton .00011. Edser gives the value .00003 for flannel, and Draper .00011 for wool and neither give values for cotton. The Smithsonian Tables (sixth edition) give .00012 for flannel, while three other well-known tables give the value .000035 with Forbes as authority. Lees obtained in 1892 for flannel the value .00023, and Lees and Chorlton in 1896 the value .00012, with no explanation of the difference. Similarly the values given for cotton vary from .00003 to .0005. It was hence suggested by Professor Laird that it would be worth while to undertake a new set of measurements of thermal conductivities of some materials used in clothing.

The method chosen was the disc method described in detail by Lees in the Philosophical Transactions of the Royal Society, A, 191, 1898. In the present experiment three copper discs, 4 cm. in diameter and approximately 3 mm. thick, were used. Copper and constantan wires were soldered at opposite ends of a diameter of each disc. Between the

first and second discs was a flat heating coil, and between the second and third discs the material to be tested made into disc form. The whole was shellacked, tied with a silk thread, and suspended in a constant temperature enclosure made from a Lavoisier ice calorimeter, with oil between the walls. A thermocouple was soldered to the inner surface of the calorimeter. The other junctions of the thermocouples were in mercury cups outside the calorimeter, the temperature of which was read on a calibrated .1° thermometer. The various thermocouples were calibrated in position; a heating wire wound around in the oil filled space between the walls of the calorimeter, and separated from the inner wall by some pieces of wood, served to raise the temperature as required.

The formula for conductivity used by Lees for this disc method, with some change in notation, is:

$$k = H \frac{(\pi r^2+2\pi r t_3)v_3+\frac{1}{2}(v_2+v_3)\pi r t_s}{(\pi r^2+2\pi r t_3)v_3+\pi r t_s(v_2+v_3)+2\pi r t_2 v_2+(\pi r^2+2\pi r t_1)v_1} \times \frac{t_s}{(v_2-v_3)\pi r^2},$$

where H = total heat supplied,

r = radius of discs,

t_1, t_2, t_3, t_s = thickness of the three copper discs and of the substance respectively,

v_1, v_2, v_3 = temperature excess of the three copper discs over the surroundings.

In computing the thickness of the discs half the thickness of the heating coil is added to the first disc and half to the second. A correction for the heat conducted along the wires of the thermocouples is also made by adding $\sqrt{qkph}/2\pi rh$, where q is the cross section, p the perimeter, k the conductivity, and h the emissivity of the wires.

In the above formula it is assumed that for the intervals used the heat emitted per square centimeter by each disc is proportional to the corresponding temperature excess, or that the emissivity is a constant. In the course of the experiments it was found that this assumption is unjustified for the temperature range used. Accordingly separate observations were made on the rate of cooling of the discs and a curve plotted with emissivity and temperature as coordinates, this method was checked later by a measurement of the steady temperature attained by the two copper discs alone for different values of the heating current. This curve gave a correction factor to be used in each case with the above formula. The emissivity at 10° and 15° temperature excess was found to be 0.000256, and 0.000276 respectively; the difference is greater than that found by McFarlane.[1] The effect of the correction is to reduce the value of the conductivity over that given by the Lees formula from

[1] Smithsonian Tables, 6th edition, p. 252.

four to seven per cent., or up to ten per cent. in extreme cases, since the numerator should be reduced by a factor h_3/h_1 nearly, where h_1 and h_3 are the emissivities at the temperatures of the corresponding discs, and only one term of the denominator is reduced. In the conditions used by Lees the difference in temperature between the two sides of the substance being tested was smaller than here, but even in some of his experiments the correction would probably amount to over two per cent., and it is possible that some of the apparant decrease in conductivity with rise in temperature observed by him was due to failure to apply such a correction.

The power was supplied from a storage cell, and was measured by a volt-ammeter method. The voltmeter and ammeter were tested by potentiometer methods. A correction was applied for the heat lost in the connecting wires. No readings were used when the temperature of a disc changed more than .1° in 15 minutes, or when the difference in temperature on the two sides of the material being tested changed more than .05° in 15 minutes. The whole difference here was from 3° to 9°, but was usually between 3° and 4°, and the temperature of the material being tested was between 30° and 40°. Lees and Chorlton[1] worked out the problem of the variation of temperature in a brass disc similarly placed, and from their solution it would appear that the temperature throughout the copper discs used in these experiments could be considered uniform. As an experimental check the one thermocouple was soldered to the top of the upper disc for a time instead of in a small hole at the side and this alteration made no perceptible change in the results.

Twelve different wearing materials, and unspun silk were tested. Five were from common knitted underwear, namely, artificial silk, linen mesh, medium weight cotton, and two kinds of woolen wear, wool no. 1 a loosely knit light weight sample, wool no. 2 a more tightly knit one. The woven materials were cotton cloth, flannelette, a closely woven wool suiting, white dress linen, and three kinds of silk dress material. Silk no. 1 was a soft dress silk, pure except for the dye, silk no. 2 tussah silk, (wild silk), silk no. 3 white parachute silk (cultivated Japanese silk). Silks nos. 2 and 3 and the unspun silk (French cocoons combed) were kindly furnished by Cheney Bros. as pure silk. The knitted materials and the cotton cloth had all been washed many times, being cut from worn articles of clothing. The others were in new condition.

Several thicknesses were generally used in making the discs. The edges were sewed together with ravellings to make a smoother surface, and were coated with shellac, melted or in solution. In a number of

[1] Phil. Mag., 41, p. 497, 1896.

instances no shellac was used with no difference in the result. In order to check the values found and to see that no error was introduced due to a constant difference of temperature between the substance and the copper, experiments were made with discs of different thickness for most of the various materials. The values agreed for small thicknesses, but as the thickness increased the values increased as illustrated by a set of values obtained for the wool suiting, 125, 114, 119, 137, and 154 $\times 10^{-6}$ with discs of one, two, three, four and six layers respectively. It is evident that the formula is not intended for use when the difference in temperature on the two sides of the substance being tested is large, since it assumes that the temperature decreases uniformly in it and that the heat conducted through may be taken as the mean of that entering and leaving the disc. A formula was worked out by assuming a simple exponential distribution of temperature in the given disc, which gave relatively smaller values for the greater thicknesses, but not sufficiently smaller to bring them into agreement with the first values, and it probably did not take into consideration all the factors involved. It is true also that the correction for the variation of emissivity with temperature is large in these cases, and makes the results more doubtful.

The discs were kept in a drying chamber with calcium chloride, and calcium chloride was placed in the calorimeter. With one of the knitted woolen samples, that by chance was not dried before using, the value .000152 was obtained instead of .000120 as found later. It was hence suggested that the effect of moisture should be investigated. For this purpose the discs were left in a moist atmosphere, and a little water was put in the bottom of the calorimeter. When the discs were heated they naturally dried somewhat, so that in the steady state there was a limit to the moisture possible. Wool with 4 per cent. moisture gave a value .000099 as against .000093 when dry, and with 8 per cent. moisture a value .000104; and for a sample of cotton the value increased from .000185 to .000191 on an average for 1.5 per cent. moisture. These increases are less than those given by Lees and Chorlton (*l.c.*), and less than that suggested by the discrepancy noted with the earlier sample. Somewhat lower values on an average were obtained for cotton, wool and silk in months when the laboratory was heated, than in the summer, but the amount of moisture must have been small at any time as fresh calcium chloride was constantly used.

In carrying out the experiments the largest source of error apart from the effects of moisture is in the measurement of the thickness of the discs. It is thought that this error would not be more than 2 per cent. The materials were generally under a pressure of 6 gm./cm.^{2}, determined by

the weight of the discs. Small constant errors in the calibration factor for the thermocouples, in the constants of the discs, and in the correction for the power used might amount to between 1 per cent. and 2 per cent. These errors would not affect the relative values. The "probable error" computed from the measurements on any one material is less than 1 per cent., except for the woven cotton where with a small number of measurements it is 2 per cent.

Table I. gives values of the conductivity obtained for knitted cotton at different times and with different samples and different thicknesses. They show fair agreement. Table II. shows in column 1 the materials used. Column 2 gives the thickness of a single layer of the material, column 3 its weight in grams per 100 sq. cm., column 4 the average value of the conductivity found not including the values for thick discs, column 5 this conductivity multiplied by the density. This latter is the flow of heat per sq. cm. per sec. for a unit difference of temperature between surfaces such that a gram of material would lie between, this may be called the conductivity per equal weight. Column 6 gives values obtained by Lees and Chorlton[1] by a slightly different method for some similar materials. The woolen materials show plainly the effect of loose texture in increasing warmth where wind is not a factor, both in the values of absolute conductivity and more strikingly in the conductivity for equal weight. The silk materials show this even more so, there being an approximately linear relation between conductivity and density, so that it should be possible to estimate the conductivity of any given sample fairly closely if the density were known. Extrapolating

TABLE I.

Cotton (Knit).

Date.	Number of Pieces.	Thickness.	Conductivity.
June 2, 1919	4	.32 cm.	.000191
June 6, 1919	8	.632 cm.	.000211
June 9, 1919	8	.632 cm.	.000212
June 9, 1919	6	.46 cm.	.000190
June 10, 1919	6	.46 cm.	.000194
July 25, 1919	4	.32 cm.	.000186
Feb. 18, 1921	4	.316 cm.	.000180
Feb. 19, 1921	4	.32 cm.	.000184
May 2, 1921	4	.32 cm.	.000180
May 5, 1921	4	.35 cm.	.000177
July 12, 1921	4	.344 cm.	.000182
July 15, 1921	4	.32 cm.	.000182
July 20, 1921	4	.32 cm.	.000184

[1] Phil. Mag., 5, 41, p. 495, 1896.

TABLE II.

Material.	Thickness per Piece.	Weight per 100 sq. cm.	Conductivity.	Conductivity × Density.	Conductivity, Lees and Chorlton.
Wool no. 1	.068 cm.	1.20 gm.	.000094	1.66×10^{-5}	
Wool no. 2	.126 "	2.65 "	.000120	2.53	.00012 (New flannel)
Wool suiting	.094 "	3.6 "	.000118	4.51	.00013 (Old flannel)
Unspun silk		.12[1] "	.000076	0.91	.0000613[2]
Silk no. 1	.0194 "	.578 "	.000101	3.00	.000095
Silk no. 2	.0138 "	.605 "	.000111	4.87	
Silk no. 3	.0138 "	.64 "	.000122	5.66	
Silk (artificial)	.045 "	.75 "	.000117	1.95	
Flannelette	.097 "	1.55 "	.000131	2.09	.00015
Cotton (woven)	.030 "	1.0 "	.000168	5.60	.00018 (Calico)
Cotton (knit)	.079 "	1.94 "	.000184	4.52	
Linen (mesh)	.098 "	2.6 "	.000158	4.19	
Linen (woven)	.033 "	1.95 "	.000167	9.87	.00021

[1] Density in gm./cm.[3] under a pressure of 6 gm./cm.[2]

[2] Rubner, Landolt and Bornstein Tables, 1905, p. 509.

however to pure silk (density 1.56) gives only about .0003 instead of .0008 as found by Rubner.[1] The advantage of wool over cotton for warmth shows up in column 5, for in considering the favorable position of flannelette, it should be recalled that the sample was new. The linen appears to have a distinctly lower conductivity than previous measurements show; one set of readings was made on an unbleached sample, of slightly less density, and a still lower value was found. From the results it may be inferred that at equal density the substances would come in the order silk, wool, artificial silk, linen, cotton, as to conductivity, and that of materials as actually found unspun silk is the warmest and woven linen the coolest, the linen changing place with cotton because of its actual greater density in manufacture.

In conclusion, the author expresses her appreciation of the aid received from Professor Laird in carrying out the experiment, and especially of the help in working out the correction of the errors involved.

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[1] Landolt and Bornstein Tables, 1905, p. 509.

VAPOR PRESSURE OF METALLIC CALCIUM.

BY NORMAN B. PILLING.

SYNOPSIS.

Vapor Pressure of Calcium, 500–700° C., from Rate of Evaporation in Vacuum.—A drawn wire of calcium was coiled into an open helix and placed in a glass tube which was then evacuated and heated to a definite temperature for a definite time. From the loss of weight due to evaporation the vapor pressure was computed by using a formula derived from the kinetic theory but involving a correction factor for the reflection of molecules by the walls of the hot tube. This factor was assumed to be a constant of the apparatus and was determined by making measurements for zinc and cadmium whose vapor pressures are known. The calcium used had 1.6 per cent. Mg and 1.25 per cent. $CaCl_2$. The values obtained for 500 to 700° C. are well represented by the formula: $\log p = 9.73 - (10{,}170/T)$, the corresponding equations for zinc and cadmium being $9.41 - (7070/T)$ and $9.02 - (5940/T)$ respectively.

Vapor Pressure of Liquid Calcium, Computed using Richards's relation between the vapor pressures of liquid and solid phases, is given by the equation $\log p = 9.27 - 9670/T$. From this equation the *boiling point* comes out 1240° C.

EXPERIMENTAL METHOD.

THE method of measurement involved the determination of the rate of evaporation of a certain weight of metallic calcium of known surface area at constant temperature and in vacuo. From this rate it is possible to compute by means of the kinetic theory of gases the equilibrium vapor pressure. In this way the vapor pressures of tungsten, molybdenum and platinum have been computed.[1]

The following expression has been derived[2] for the vapor pressure of a substance in terms of its rate of evaporation in vacuum:

$$m = \sqrt{\frac{M}{2\pi RT}} \cdot p, \qquad (1)$$

in which

M = molecular weight of vapor (assume metallic vapors to be monatomic).
R = gas constant = 8.32×10^7 ergs/degree.
T = absolute temperature.
p = pressure, dynes/cm.^{2}
m = rate of evaporation, gm./(cm.^{2} sec.).

[1] I. Langmuir, Vapor Pressure of Metallic Tungsten, PHYS. REV., II., Vol. 2, p. 329, 1913. I. Langmuir and C. M. J. Mackay, Vapor Pressure of the Metals Platinum and Molybdenum, PHYS. REV., II., vol. 4, p. 377, 1914.

[2] I. Langmuir, Vapor Pressure of Metallic Tungsten, PHYS. REV., II., Vol. 2, p. 329, 1913.

This expression is valid when the following postulates hold

1. That at low vapor pressures (few millimeters) the mutual interference between vapor molecules is so slight as to make the rate of evaporation a function of temperature only and independent of the external pressure.

2. That the rate of condensation is proportional to the vapor pressure.

3. That the coefficient of reflection with respect to both metal surface and enveloping walls is zero.

The above equation then willgive the rate of evaporation in a vacuous space whose enveloping walls are cold or remotely distant. As will be shown later, in the experimental arrangement adopted the enveloping walls have been made neither remotenor cold, and hence another factor, the reflection of calcium molecules from this enveloping surface back to the metallic surface with consequent condensation has to be taken into account.

Let s = coefficient of reflection from the enveloping walls. Then

$$m = \sqrt{\frac{M}{2\pi RT}} \cdot p(1 - s). \qquad (2)$$

Solving for p, and changing p from dynes/cm.^{2} to millimeters of mercury (1 mm. Hg = 1333 dynes/cm.^{2})

$$\log p = \log m + \tfrac{1}{2} \log T + \tfrac{1}{2} \log \frac{2\pi R}{M} - \log (1 - s) - 3.125. \qquad (3)$$

Details of the experimental method used are shown in the apparatus diagram (Fig. 1). A 19/32″ bore pyrex glass tube closed at the bottom extended to the middle of a vertical electrically heated tube resistance furnace. This ignition tube was connected to a standard set of mercury diffusion pumps through a greased stopcock; a liquid air trap was placed between the stopcock and the furnace to prevent vapors from the lubricant of the cock and mercury from the pumps diffusing back into the ignition tube. The calcium in the form of a drawn wire helix was cleaned, weighed and immediately dropped into the ignition tube through a suitable opening at the top. In its initial position (Fig. 1) the helix

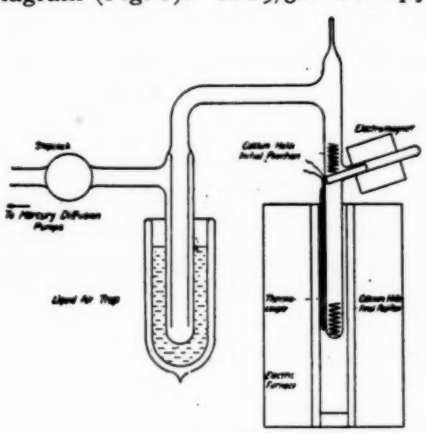

Fig. 1.

rested on a steel pin which projected across the heating tube from an inclined lateral tube above the top of the furnace. As soon as the specimen was in place the top of the heating tube was sealed off and the entire system was evacuated. A platinum-platinrhodium thermocouple within a slender quartz protection tube was lashed to the outside of the glass tube with asbestos tape. When the furnace had reached a steady temperature and time had been given for the removal of absorbed moisture, etc., from the inside of the tube, the steel pin was withdrawn with an external electromagnet and the calcium helix dropped into the furnace. At the end of the run, the furnace was lowered away from the ignition tube, and the calcium cooled in vacuo. When cold, the tube was cracked open and the loss in weight of the calcium helix determined.

At temperatures above 600° C. the pyrex glass collapsed. A somewhat larger tube was then used, into which an unglazed usalite porcelain liner, 19/32″ bore, was slipped, which acted as a support for the softened glass.

In all cases except cadmium the evaporated metal condensed as a mirror at the mouth of the furnace. The cadmium condensed just below the furnace mouth.

Determination of Coefficient of Reflection.

In evaluating the coefficient of reflection, the rates of evaporation of several metals with known vapor pressures were measured under various conditions, from which the coefficient was computed by substitution in equation (2). A search of the vapor pressure literature showed the data to be very incomplete and unsatisfactory regarding values of the vapor pressures of the solid metals. Almost all of the data are based on extrapolated curves from the liquid state, oftentimes with the weight of very few measurements.

The vapor pressure of solid zinc and solid cadmium has been measured over a considerable temperature range by a dynamic method by Egerton.[1] Accordingly equations were deduced from his data which were used as standards of reference in measuring the reflection coefficient with zinc and cadmium. These equations follow.

$$\text{Zinc:} \qquad \log p = -\frac{7070}{T} + 9.41,$$

$$\text{Cadmium:} \quad \log p = -\frac{5940}{T} + 9.02.$$

The zinc which was used in this determination was 0.124 cm. diameter Horse Head brand zinc wire furnished drawn to size by the New Jersey

[1] A. C. Egerton, Vapor Pressure of Zinc, Cadmium and Mercury, Phil. Mag., Vol. 33, p. 33, 1917.

Composition of Zinc and Cadmium Wire.

	Zn	Cd	Fe	Pb	As
Zinc (no. 077).....	99.94(*d*)	nil	.01	.05	——
Cadmium (no. 075)	nil	99.99(*d*)	——	nil	.006

d = by difference.

TABLE I.

Coefficient of Reflection, Zinc and Cadmium Vapor.

Metal.	No.	Temperature, °C.	Ignition Tube Reflect. Surf.	Vapor Pressure, mm.	*s*	log (1 − *s*)
Zinc.....	3558	301	Pyrex glass.....	.00133	.99369	−2.200
	3556	404	Pyrex glass.....	.0813	.99230	−2.113
	3557	405	Pyrex glass.....	.0840	.99236	−2.117
	3582	402	Usalite porcelain	.0759	.99198	−2.096
Cadmium...	3559	302	Pyrex glass.....	.0488	.99213	−2.104

Zinc Company. The cadmium was a rod rolled and drawn to wire 0.103 cm. diameter in the laboratory.

Upon examination of this table it will be seen that within the limits of experimental error the coefficient of reflection is a very large but constant quantity, practically independent of temperature, nature of reflecting surface (glass or porcelain) and vapor (metal). The experimental error was largest with no. 3558; the mean value of the four other measurements of log (1 − *s*) is − 2.107, which was taken as a characteristic constant of the apparatus and used in the reduction of data on calcium.

VAPOR PRESSURE OF CALCIUM.

The calcium metal with which the following determinations were made was a laboratory product prepared electrolytically by Mr. P. H. Brace.[1] This was forged, rolled and drawn cold to wire 0.106 cm. diameter, and stored for use in Lectroseal oil. Analysis of a large piece of the undrawn material follows.

Analysis of Calcium. No. 092.

Ca.....	97.16
Mg.....	1.62
Fe.....	0.009
$CaCl_2$.....	1.25
	100.04

[1] See P. H. Brace, Transactions, American Electro-chemical Society, 1920, p. 69.

In preparing the wire for use, a measured length was coiled into an open helix 8 mm. diameter. The oil was removed by soaking in xylene, and the crust of calcium salt on the surface removed by pickling in dilute hydrochloric acid in alcohol. When the surface was bright, the acid was rinsed off in alcohol, the alcohol removed by momentary immersion in ether, which attacked the metal vigorously, and then dried quickly in air. The wire diameter was then measured, the helix weighed, placed in the apparatus and sealed off as soon as possible.

TABLE II.

Rate of Evaporation of Calcium.

No.	Temperature ° C.	Specimen.		Weight of Calcium Evaporated, gm.	Time, min.	Rate of Evaporation, gm./(cm². sec).
		Weight, gm.	Surface Area, cm².			
3448	503	0.3694	10.8	0.0024	64	0.058×10^{-6}
3452	553	0.9312	25.8	0.0267	76	0.227
3451	605	0.4414	11.7	0.0366	58	0.900
3449	608	0.4460	12.7	0.0413	50	1.08
3456	652	0.5696	13.5	0.0843	18	5.78
3457	700	0.5689	13.1	0.1621	12.5	15.9

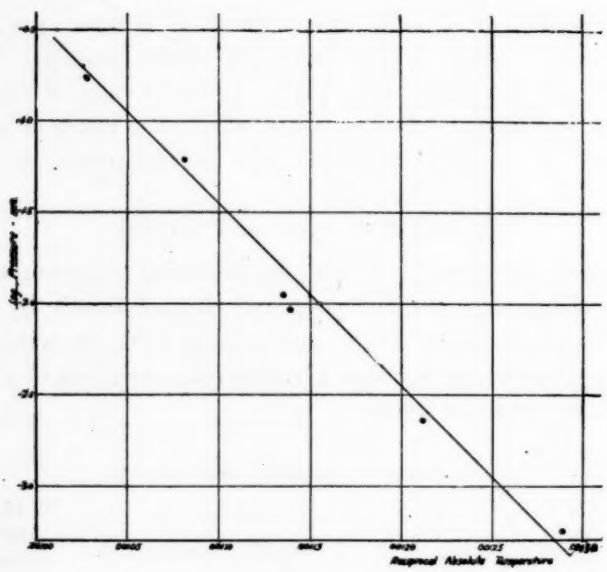

Fig. 2.

Experimental data have been obtained for the temperature range 500–700° C.

TABLE III.

Vapor Pressure of Calcium.

No.	Temperature, °C.	Pressure, mm. Hg.
3448	503	.000561
3452	553	.00227
3451	605	.00931
3449	608	.0112
3456	652	.0614
3457	700	.173

The experimentally determined values of vapor pressure are plotted in Fig. 2, the coördinates being log pressure and reciprocal absolute temperature. The relation is linear, and the best straight line is

$$\log p = -\frac{10{,}170}{T} + 9.73, \qquad (4)$$

representing the vapor pressure of solid calcium. Richards[1] making use of the Clausius-Clapeyron equation and Richards's rule, has derived a relation between the vapor pressure of the solid and liquid phases which has experimental verification for several substances. If the vapor pressure curves are expressed

$$\log p = -\frac{A}{T} + B \text{ (solid)}$$

and

$$\log p = -\frac{A'}{T} + B' \text{ (liquid)},$$

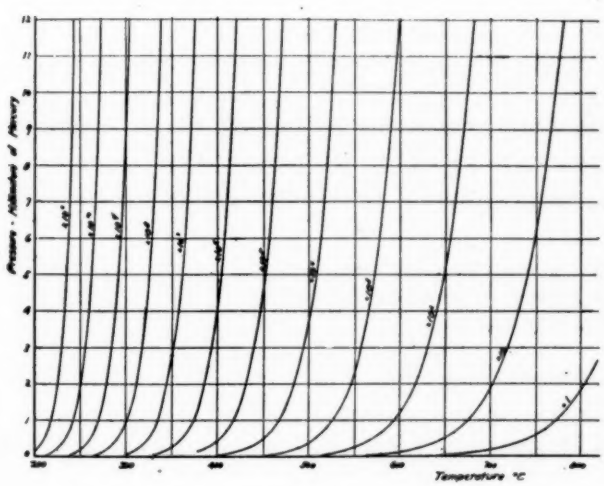

Fig. 3.
Vapor Pressure of Solid Calcium.

[1] J. W. Richards, The Vapor Tensions of the Metals, Journal Franklin Institute, Vol. 187, p. 581, 1919.

the relation between the four constants is as follows:

$$A' = A - 0.46\ Tm.p.$$
$$B' = B - 0.46.$$

Taking the melting point of calcium to be 805° C.[1]

$$\log p = -\frac{9670}{T} + 9.27, \qquad (5)$$

the vapor pressure curve for liquid calcium.

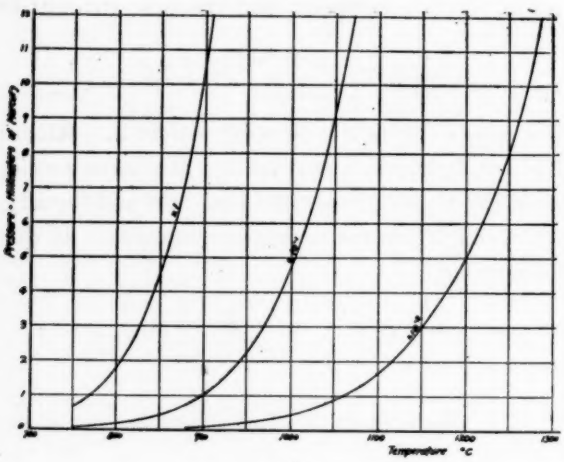

Fig. 4.

Vapor Pressure of Liquid Calcium.

Charts representing equations (4) and (5), the vapor pressures of solid and liquid calcium respectively, are given in Figs. 3 and 4.

From the vapor pressure curves the following constants may be computed.

Normal boiling point, 760 mm. . . . . 1240° C
Vapor pressure at melting point, 805° C. . . . . 2.0 mm.
Heat of vaporization

Trouton's rule $\frac{23T}{\text{At.Wt.}}$ . . . . . 867 cal./gm

Clapeyron eq. $\frac{4.57A'}{\text{At.Wt.}}$ . . . . . 1100 cal./gm

WESTINGHOUSE RESEARCH LABORATORY,
EAST PITTSBURGH, PA.,
May 24, 1921.

[1] Soc. Franc. de Physique, p. 258.

LIGHT EMISSION FROM A MOVING SOURCE IN CONNECTION WITH THE RELATIVITY THEORY.

By N. Rashevsky.

Synopsis.

Light Emission from a Moving Source; a Generalized Explanation of the Michelson-Morley Experiment.—The paper is based upon unpublished work left by the late *Nikolas Pashsky* of Kieff. It is pointed out that the experiment does not prove the constancy of the velocity of light but merely that if light is sent out in all directions from the center of a spherical mirror, all rays after reflection will return simultaneously to the center no matter what the velocity of the system through space. This result requires merely that with respect to axes moving with the source, the velocity of light in a direction making an angle φ with the direction of motion is given by $\sigma_\varphi = \sigma/\{1 + \sqrt{[\psi \cos \varphi/(\sigma + \psi)]}\}$, when σ and ψ are arbitrary functions of the velocity of translation v, with the only conditions that for $v = 0$, $\psi = 0$ and $\sigma = c$. There are therefore an *infinite number of possible hypotheses* which will explain the experiment, *in addition to the relativity theory*, which assumes that σ_φ = constant. The only way to decide the matter would be to measure the velocity of light by a method in which the ray of light would not return to its starting point.

THE following paper is based upon the unpublished works of Nikolas Pashsky, late assistant in physics at the University of Kieff.[1] His manuscripts were entrusted to me by his widow to prepare for publication, but I was forced to leave them in Kieff.

Wishing to delay no longer in presenting his ideas to the scientific world I am presenting my own explanation of some of his ideas.

The present paper represents only a very small portion of the large mass of work which he had nearly ready for publication.

1. The classical theory of the electromagnetic field, among other fundamental statements, on which it is based, contains the following postulate:

(*a*) The velocity of propagation of any electromagnetic disturbance in free space is independent of the motion of the source, and is, relative to a system at rest, equal to $c = 3 \times 10^{10}$ cm./sec.

Einstein, denying *the reality of absolute rest* and *absolute motion* and requiring that the velocity of light should have the same value c, relative to any chosen system, came to the familiar conclusions, which all together form the relativity theory.

The principal experimental fact, on which are based his speculations, is the Michelson experiment, to which however the relativity theory

[1] Died June 26, 1918, aged 32 years.

must ascribe more than it gives in reality. According to this theory the velocity of light in a moving system is in all directions equal to c, *i.e.*, all the points of a sphere, from the center of which at the moment t an electromagnetic disturbance is sent out, will receive the impulse simultaneously, while the Michelson experiment shows only that all those disturbances, reflected by the points of the sphere, will *come back to the center simultaneously*, and this is not the same.

H. Lorentz, wishing to give an explanation for this true result of the Michelson experiment, made the contraction hypothesis. Einstein, going beyond the limits of the experiment and requiring the simultaneity of the arrival of impulses on the sphere, was *forced* to make the assumption as to the change of time-units in the moving system.

The purpose of this article is to show that without going further than the experiment leads us, and consequently abandoning the principle of relativity, we can, without making the contraction assumption, find an infinite number of hypotheses satisfying the Michelson experiment and that all the theories based on those hypotheses are equivalent one to another and to a *certain extent* equivalent to the relativity theory. But for this purpose *we must abandon the postulate I of the constancy of velocity of light.*

Such an attempt was made by W. Ritz, who made the assumption that the velocity of light emitted by a moving source is equal, relative to a system at rest, to $c + v$ and $c - v$ respectively in the direction of movement of the source and opposite it, where v is the velocity of translation. We shall now make a more general assumption.

(*b*) The velocity of light emitted by a moving source is equal, relative to a system of rest, to $c + f_1(v)$ in the direction of motion and $c + f_2(v)$ in the opposite direction, where $f_1(v)$ and $f_2(v)$ are arbitrary functions of v, with the only limiting condition that

$$f_1(0) = f_2(0) = 0. \tag{1}$$

Relative to axes moving with the source the velocities will be respectively

$$\begin{aligned} c + v + f_1(v) &= U_1(v) = \sigma + F_1(v), \\ c - v + f_2(v) &= U_2(v) = \sigma + F_2(v), \end{aligned} \tag{2}$$

where σ is a function of v with the condition $\sigma(0) = c$; and $F_1(v)$ and $F_2(v)$ are other arbitrary functions of v with the same limiting conditions

$$F_1(0) = F_2(0) = 0.$$

Here it will be of use to define what we understand by the words "velocity of light."

All the methods employed up to the present to measure this velocity are based on the principle of Fizeaux or Foucault in both of which the

light travels along a path of a known length, and comes back again in the opposite direction. The time necessary to traverse this path is measured, and the velocity is obtained from the equation

$$T = \frac{2l}{\sigma},$$

where l is the length of the path. It is obvious that this does not give us in any case the "true" velocity of light, for the velocities in opposite directions may be different. The velocity obtained in this way we shall denote as "measured velocity" of light, in distinction to the "true velocity" which could be obtained by a method using the propagation of light in one direction. But in all our physical experiments we know only the "measured velocity," a fact which is of importance. Now we shall make the assumption that σ is the "measured velocity" of light in our moving system. But, as our hypothesis must satisfy the conditions of the Michelson experiment, we must require that the time necessary for light to pass from a moving point A to another point B, situated at the distance l from A and moving with it, and return to A, must be independent of whether the system is moving in the direction AB or BA and equal to σ.

Hence

$$\frac{l}{\sigma + F_1(v)} + \frac{l}{\sigma + F_2(v)} = \frac{2l}{\sigma}, \tag{3}$$

or, after some transformations,

$$-\frac{\sigma}{2}[F_1(v) + F_2(v)] = F_1(v)F_2(v). \tag{4}$$

If we put

$$F_1(v) + F_2(v) = 2\psi(v), \tag{5}$$

where $\psi(v)$ is an arbitrary function with the same limiting condition

$$\psi(0) = 0,$$

we have

$$\begin{aligned} -\sigma\psi(v) &= F_1(v)F_2(v), \\ 2\psi(v) &= F_1(v) + F_2(v); \end{aligned} \tag{6}$$

we see that $F_1(v)$ and $F_2(v)$ are roots of the quadratic equation

$$-F^2 + 2\psi(v)F + \sigma\psi(v) = 0.$$

Hence

$$\begin{aligned} F_1(v) &= \psi(v) + \sqrt{\psi^2(v) + \sigma\psi(v)}, \\ F_2(v) &= \psi(v) - \sqrt{\psi^2(v) + \sigma\psi(v)}, \end{aligned} \tag{7}$$

and for the velocities relative to a moving system we find respectively

$$\sigma + \psi(v) + \sqrt{\psi^2(v) + \sigma\psi(v)}$$

and (8)

$$\sigma + \psi(v) - \sqrt{\psi^2(v) + \sigma\psi(v)}.$$

But from (3) we see that we can change the rôles of the functions $F_1(v)$ and $F_2(v)$ and so finally we get

$$\begin{aligned} &\sigma + \psi(v) \pm \sqrt{\psi^2(v) + \sigma\psi(v)}, \\ &\sigma + \psi(v) \mp \sqrt{\psi^2(v) + \sigma\psi(v)}. \end{aligned} \tag{9}$$

So far we have neglected the velocity of light in a direction making a definite angle with the direction of translation. We may show that we obtain a result consistent with the Michelson experiment if we assume that the hodograph of velocities relative to moving axes is an ellipsoid of revolution along the major axis, this axis being parallel to the direction of motion, and the source being situated in one of the foci of the ellipsoid. The velocities along the axis of revolution are given by (9).

Then we have for the major semi-axis

$$a = \sigma + \psi(v), \tag{10}$$

the linear excentricity is

$$e = \sqrt{\psi^2(v) + \sigma\psi(v)}, \tag{10a}$$

the parameter which gives the velocity in a direction perpendicular to the direction of motion is

$$p = \sigma. \tag{10b}$$

The numerical excentricity is

$$\frac{e}{a} = \sqrt{\frac{\psi(v)}{\sigma + \psi(v)}}. \tag{10c}$$

Hence the velocity of light in a direction making an angle φ with the line of motion is

$$\sigma_\phi = \frac{\sigma}{1 \pm \sqrt{\dfrac{\psi(v)}{\sigma + \psi(v)}} \cos\varphi}. \tag{11}$$

The positive sign in the denominator corresponds to the assumption that the source lies in the front focus; and the negative that it lies in the rear one.

It is easy to show that our assumption explains the Michelson experiment, if we make the assumption that every point of the reflecting sphere behaves like an independent source, emitting light in accordance with (11).

Really the time necessary for the light to pass from the center to a point of the sphere, situated in a direction defined by the angle φ is, if l = radius of the sphere,

$$T_1 = \frac{l}{\sigma_\phi} = \frac{l\left(1 \pm \sqrt{\frac{\psi(v)}{\sigma + \psi(v)}} \cos \varphi\right)}{\sigma}.$$

The time necessary to return by the same path from the sphere to the center is

$$T_2 = \frac{l}{\sigma_{\pi+\phi}} = \frac{l\left(1 \mp \sqrt{\frac{\psi(v)}{\sigma + \psi(v)}} \cos \varphi\right)}{\sigma}.$$

The change of sign before the radical is due to the fact that

$$\cos(\pi + \varphi) = -\cos \varphi.$$

The entire time necessary for the light to go and return is

$$T = T_1 + T_2 = \frac{2l}{\sigma}, \tag{12}$$

i.e., independent of the direction of propagation.

Formula (12) shows also that if we measure the velocity of light by ordinary methods, sending the beams twice by the same path and dividing the double length of the path by the time that is necessary for the light to go and return, we will always obtain the value σ. If σ is independent of the velocity of translation of the source, and σ = const. = c, then we will never detect in this manner the absolute movement of the system.

If σ is a function of v, this would be possible.

As $\psi(v)$ is a quite arbitrary function, only limited by the condition

$$\psi(0) = 0,$$

we have thus found an infinite number of solutions of the "Michelson problem," all equivalent one to another.

2. To show now the mutual relation between our theory and the relativity theory, we may proceed as follows:

Let us consider a sphere of radius l, moving with a uniform velocity v.

Let the center of the sphere be the origin of moving coördinate axes and let the x-axis lie in the direction of motion. Let us consider now the phenomena of light propagation from the point of view of the classical theory.

The velocity of light referred to the moving axes will be, as easily shown, respectively $c - v$ and $c + v$ in the direction of motion, and $\sqrt{c^2 - v^2}$ in a direction perpendicular to this. The time necessary for the light to travel from the center of the sphere and back will be in the latter case

$$\frac{2l}{\sqrt{c^2 - v^2}}, \tag{13}$$

and in the former

$$\frac{l}{c+v}+\frac{l}{c-v}=\frac{2lc}{c^2-v^2}, \tag{14}$$

i.e., if this time is greater, and if we desire to maintain the simultaneity of return of light to the center, we *must* assume that l is contracted along the line of motion in the ratio

$$\frac{\sqrt{c^2-v^2}}{c}=\sqrt{1-\frac{v^2}{c^2}} \quad \text{(assumption 1)},$$

and then it is easily shown that the time of return of light to the center will be independent of the direction of propagation.

This would account for the Michelson experiment and, as Lorentz showed, for all the other known experimental phenomena.

But Einstein, as remarked above, went further and postulated, that the "measured velocity" of light in a moving system should be c; as in our case it is equal to

$$\sqrt{c^2-v^2},$$

there remains nothing but to make the assumption that in the moving system time runs slower in a ratio

$$\frac{\sqrt{c^2-v^2}}{c}=\sqrt{1-\frac{v^2}{c^2}} \quad \text{(assumption 2)},$$

for then the time required for light to go and return will be not

$$\frac{2l'}{\sqrt{c^2-v^2}} \quad \text{but} \quad \frac{2l'}{c}.$$

But even if we make this assumption we will find that the absolute movement of the system could be detected, for, though the time of return of the light to the center and its measured velocity are independent of the direction of propagation, the time of arrival of light at the sphere and the "true velocity" will depend upon this direction, and to remove this difficulty, we must assume that a watch whose x-coördinate is equal to x', shows the time $t-(u/c^2)x'$, if t is the time at the center (assumption 3).

In this way we obtain the complete set of assumptions which form the basis of relativity theory.

Let us now return to our hypothesis. Formula (11) without any contraction hypothesis satisfies the conditions of the Michelson experiment and shows that the measured velocity of light is independent of the direction of propagation. Thus our hypothesis is equivalent to the contraction one and furnishes an equally good explanation of all the

known experimental facts, our infinite set of assumptions giving the same result as the contraction hypothesis. All the experiments made up to the present had to do with the propagation of light in a closed path, this being true also for experiments of electromagnetic character, where we always have to do with "mutual actions" of two charges. No experiment has been made that shows the necessity of assumptions 2 and 3. They are beyond the limits of experiment. And in the same way, as between the modified Lorentz theory and the relativity theory of Einstein the only decisive experiment would be to measure the velocity of light by a method involving its propagation in one direction only; our assumptions are *to this extent* equivalent to the relativity theory.

If we should postulate the simultaneity of arrival of the light impulses at the surface of the sphere in our theory, we should be obliged to assume that the watch on the surface of the sphere shows a time

$$t' = t \mp \frac{k}{\sigma} x, \tag{15}$$

where x is its moving coördinate and

$$k = \sqrt{\frac{\psi(v)}{\sigma + \psi(v)}}. \tag{16}$$

In reality the time necessary for the light to pass from the center to a point of the sphere is equal to

$$\frac{l(1 \pm k \cos \varphi)}{\sigma},$$

and if we introduce t', it becomes

$$\frac{l(1 \pm k \cos \varphi)}{\sigma} \mp \frac{k}{\sigma} l \cos \varphi = \frac{l}{\sigma},$$

i.e., the velocity of light measured by a "one direction method" will be σ.

Of course, if we desire that even from a source at rest the velocity of light in the moving system should be σ, we must change in an appropriate manner the unit of time in our moving system.

But, without this assumption, since all the apparatus with which we make our measurements has the same velocity of translation as the earth, we shall find (applying the principle used in the deduction of 12) for the "measured velocity" of light even from extra-terrestrial sources the value σ.

If by astronomical methods, given by de Sitter and others, we obtain a constant value of the velocity of light, even from extra-terrestrial sources,[1] it does not disprove our theory; it shows only that the value of $\psi(v)$ for a given v is below a certain limit, for example

[1] By "one-direction method."

$$\psi(v) < \frac{v^2}{c^2}, \text{ etc.}$$

It will be the problem of experimental physics to find out the precise form of $(\psi(v))$.

By applying the Huygens principle and taking instead of spherical elementary waves, ellipsoidal ones, all the optics of moving systems can be built up. This was done by the late N. Pashsky. Those results I hope to publish later.

In conclusion I wish to express my sincerest thanks to Dr. P. H. Dike for the revision of the English translation of the Russian original manuscript, and for many critical remarks.

PHYSICAL LABORATORY,
ROBERT COLLEGE,
CONSTANTINOPLE,
February, 1921.

A NOTE ON THE PLANE WAVE IN AN ISOTROPIC DIELECTRIC.

By Satyendra Ray.

Synopsis.

Electric and Magnetic Forces in the Direction of Propagation of a Plane Wave in an Isotropic Dielectric need not be zero if the ether has a constant electric density P_e and a constant magnetic density P_m, for it is shown that these forces are equal, respectively, to $P_e\lambda/k$ and $P_m\lambda/\mu$ where λ, k and μ denote wave-length, inductivity and permeability respectively.

An Application of Dimensions.—The equations of a plane wave, referred to an axis of Z parallel to the direction of propagation, are,

$$\begin{aligned} K\frac{dE_x}{dt} &= -\frac{dM_y}{dz}; & K\frac{dE_y}{dt} &= \frac{dM_x}{dz}; & K\frac{dE_z}{dt} &= 0; \\ \mu\frac{dM_x}{dt} &= \frac{dE_y}{dz}; & \mu\frac{dM_y}{dt} &= -\frac{dE_x}{dz}; & \mu\frac{dM_z}{dt} &= 0. \end{aligned} \qquad (1)$$

The solution of the third and the sixth equations above gives

$$E_z = \text{constant}; \quad M_z = \text{constant},$$

instead of $E_z = 0$, $M_z = 0$, as usually stated in text-books.

In a paper on the equivalent shell of a circular current[1] a radius of the electric particle infinitely smaller than 10^{-13} cm. has been found. If it is taken to be the diameter of the electric particles of which the ether is composed an expression for the constant forces in the direction of propagation can be obtained in terms of the constants of the ether and the plane wave by the method of dimensions.

The electric force will be a function of the electric density ρ_e and inductivity K of the medium and of the wave-length Λ of the disturbance if it is periodic.

$$E_z = c\frac{\rho_e\Lambda}{K}$$

is such a function, where c is a numerical constant, and

$$[E_z] = \left[\frac{\rho_e\Lambda}{K}\right]$$

dimensionally. Similarly, assuming magnetic density ρ_m,

$$M_z = c\frac{\rho_m\Lambda}{\mu}.$$

[1] Phil. Mag., Jan., 1920.

To find the constant c. For any electromagnetic disturbance,

$$\begin{aligned}
\frac{\mu K}{c^2}\cdot\frac{d^2E_x}{dt^2} &= \frac{d^2E_x}{dx^2}+\frac{d^2E_x}{dy^2}+\frac{d^2E_x}{dz^2}-\frac{d}{dx}\left(\frac{dE_x}{dx}+\frac{dE_y}{dy}+\frac{dE_z}{dz}\right);\\
\frac{\mu K}{c^2}\cdot\frac{d^2E_y}{dt^2} &= \frac{d^2E_y}{dx^2}+\frac{d^2E_y}{dy^2}+\frac{d^2E_y}{dz^2}-\frac{d}{dy}\left(\frac{dE_x}{dx}+\frac{dE_y}{dy}+\frac{dE_z}{dz}\right); \qquad (2)\\
\frac{\mu K}{c^2}\cdot\frac{d^2E_z}{dt^2} &= \frac{d^2E_z}{dx^2}+\frac{d^2E_z}{dy^2}+\frac{d^2E_z}{dz^2}-\frac{d}{dz}\left(\frac{dE_x}{dx}+\frac{dE_y}{dy}+\frac{dE_z}{dz}\right).
\end{aligned}$$

with three similar equations in M_x, M_y, M_z; also,

$$\left(\frac{dE_x}{dx}+\frac{dE_y}{dy}+\frac{dE_z}{dz}\right)=\frac{4\pi\rho_e}{K}$$

$$\left(\frac{dM_x}{dx}+\frac{dM_y}{dy}+\frac{dM_z}{dz}\right)=\frac{4\pi\rho_m}{\mu}.$$

The equations (2) reduce to the usual form

$$\frac{\mu K}{c^2}\cdot\frac{d^2E_x}{dt^2}=\nabla^2E_x, \text{ etc.},$$

and

$$\frac{\mu K}{c^2}\cdot\frac{d^2M_x}{dt^2}=\nabla^2M_x, \text{ etc.},$$

only on condition that ρ_e and ρ_m are absolute constants, independent of both time as well as position.

For a plane wave of period τ we write

$$\begin{aligned}
E_x &= \lambda A e^{i\frac{2\pi}{\tau}\left(t-\frac{lx+my+nz}{V}\right)};\\
E_y &= \mu A e^{i\frac{2\pi}{\tau}\left(t-\frac{lx+my+nz}{V}\right)};\\
E_z &= \nu A e^{i\frac{2\pi}{\tau}\left(t-\frac{lx+my+nz}{V}\right)},
\end{aligned}$$

where l, m, n are the direction cosines of the normal to the wave front, and λ, μ, ν of the electric vector.

Differentiating the equations with respect to x, y, z, respectively and adding, we have

$$\begin{aligned}
\frac{4\pi\rho_e}{K} &= -i\frac{2\pi}{\Lambda}Ae^{i\frac{2\pi}{\tau}\left(t-\frac{lx+my+nz}{V}\right)}+(l\lambda+m\mu+n\nu)\\
&= \frac{2\pi}{\Lambda}A\sin\frac{2\pi}{\tau}\left(t-\frac{lx+my+nz}{V}\right)\cos\varphi,
\end{aligned}$$

where φ is the angle between the electric vector and the direction of propagation.

Or

$$A\sin\frac{2\pi}{\tau}\left(t-\frac{lx+my+nz}{V}\right)\cos\varphi=\frac{2\rho_e\Lambda}{K}.$$

It will be noticed the left-hand expression is the electric force in the direction of propagation and is equal to the constant $2\rho_e\Lambda/K$. A similar expression in ρ_m, Λ, μ would be obtained for the steady magnetic force in the direction of propagation. Maxwell distinctly indicates the existence of such steady forces in addition to the periodic effects.[1]

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[1] Vide Vol. II., § 783.

NOTE ON RADIATION PRESSURE.

BY R. N. GHOSH AND N. K. SUR.

SYNOPSIS.

Derivation of the Formula for Radiation Pressure.—Larmor's formula was derived on the assumption that the energy density of the radiation is proportional to $1/\lambda^2$. The same formula is now derived *for a pulse with an energy distribution in accordance with Wien's law.* If the reflector is moving toward the source with a speed v and if we assume that the amplitude for each component part of the incident pulse is unchanged by reflection, then because of the change of wave-length on reflection (Doppler effect) there is a change in energy density per second which is equal to the corresponding radiation pressure times v. Hence $p_\lambda = 2e_\lambda(c+v)/(c-v)$ and the total pressure is $2I(c+v)/c(c-v)$, when I is the intensity of the total radiation.

INTRODUCTION.

TO Larmor is due a method of argument to show that any wave motion in which the energy density is inversely proportional to the square of wave-length will exert a pressure which is equal to the energy density in the beam. His method of argument has been applied by Edser[1] to Electromagnetic waves. He on the principles of moving electric field laid down by Heaviside, arrives at the conclusion that the amplitude of the wave must undergo a change given by the formula

$$a/a' = c - v/c + v, \tag{1}$$

(1) where a and a' are the amplitudes before and after reflection. And the pressure is given by

$$p = 2E_1\{(c+v)/(c-v)\}. \tag{2}$$

(2) Where c and v are the velocities of light and reflector respectively, and E_1 is the energy density in the incident beam.

But Prof. Larmor[2] finds that he cannot accept the result contained in (1) on the mode of identification of the magnetic force with the velocity of displacement of the medium (ether).

Wiener has shown that the surface of a stationary reflector is a node, and if we assume that this condition holds good when the reflector is moving with a constant velocity, then the pressure of radiation can be demonstrated, on the basis of argument given by Larmor, when the amplitude is a complicated function of wave-length. The particular case when the energy density of the wave motion obeys Wien's or

[1] Edser, Phil. Mag., Oct., 1914. (See also Hargreaves Phil. Mag., June, 1920.)

[2] Larmor, Phil. Mag., Nov., 1914.

Planck's law of distribution of energy has been discussed in this paper, and the pressure has been found to agree with Larmor's result.

II. Sound Waves.

That sound waves exert a pressure follows readily from Larmor's theorem. The late Lord Rayleigh[1] discussed the question of pressure of Sound waves in several papers. He came to the conclusion that Sound waves of finite amplitude exert no pressure, if they are to preserve their form unchanged. Recently it has been shown by Elder Bartel[2] that such waves exert a pressure, which is not zero by taking into account the disturbance in the medium by producing the moving reflector.

III. Light Waves.

The late Lord Rayleigh[3] showed that a type of pulse given by $y = e^{-c^2x^2}$ was suitable for white light representation, and which at that time agreed with the energy distribution law of Weber. Recently Dr. Houston[4] has discussed in two papers a type of pulse which account for the various properties of white light. His pulse is given by

$$y = \frac{A \cos (5/2 \tan^{-1} x/h)}{(x^2 + h^2)^{5/4}}. \tag{3}$$

Expression (3) can be transformed into

$$y = \frac{4A}{3\sqrt{\pi}} \int_0^\infty \alpha^{3/2} e^{-h\alpha} \cos \alpha x d\alpha,$$

where $\alpha = 2\pi/\lambda$. It shows the component waves present in the pulse. They have a physical significance when the pulse passes through a dispersive medium. The amplitude of a component wave λ is given by

$$A_\lambda = \frac{4A}{3\sqrt{\pi}} e^{-h\alpha} \cdot \alpha^{3/2}.$$

So that the amplitude is a function of the wave-length.

The energy density $E_\lambda d\lambda$ comprised between λ and $\lambda + d\lambda$ is given by

$$E_\lambda d\lambda = \frac{c_2 A^2}{\lambda^5} e^{-4\pi h/\lambda} d\lambda$$

where c_2 is a constant. Now if we identify h as the reciprocal of absolute

[1] Lord Rayleigh, 1905, pp. 364, 1902, pp. 338, Phil. Mag.

[2] Edler Barter, Proceedings of the Asiatic Society of Bengal, Nov., 1919. See also Warren Weaver, Phys. Rev., May, 1920.

[3] Scientific Papers, Vol. III., p. 268.

[4] Houston, Proceedings of the Royal Society, 1913, p. 339; 1914, p. 288.

temperature corresponding to the radiation we have

$$E_\lambda = \frac{c_2 A^2}{\lambda^5} e^{-4\pi/\lambda T} = \frac{c_2 A^2}{\lambda^5} e^{-c_1/\lambda T},$$

which is Wien's Law.

Now let us apply Larmor's argument to the pulse given by (3) incident normally on a perfect reflecting surface. The reflector is moving with a velocity v in opposite direction to that of the incident pulse. By Doppler's principle the component wave of length λ is changed into λ' so that

$$\frac{\lambda}{\lambda'} = \frac{c+v}{c-v}. \tag{4}$$

The amplitude A_λ before reflection is proportional to

$$A e^{-c_1/\lambda T}/\lambda^{3/2},$$

and after reflection it must remain the same, so that the surface of the reflector may be a node. Therefore A is changed in such a way so as to fulfill this condition given by

$$\frac{A'}{A} = \left(\frac{c-v}{c+v}\right)^{3/2}$$

in accordance with Wien's displacement law.

The change of A is connected in some manner with the disturbance in the ether produced by the moving mirror not known at present. Dr. Green[1] in a very recent paper on the "Fluid analogue of the ether" has discussed the properties of the ether in the light of the ordinary fluid. By pushing the analogy a little further, we may conceive that similar disturbance may occur in the ether, as in the ordinary fluid when a plane lamina moves through it with a constant velocity. If pulses travelling with the minimum velocity are incident upon the lamina, they are reflected back, but near the lamina, the disturbance will be the sum of the disturbances produced by the pulses and the motion of the lamina, the surface of the lamina always being a node. Another point to be noticed is the pressure experienced by the lamina. It will again be sum of the pressures due to the pulses, and the additional pressure depends upon the velocity of the lamina. This is precisely the pressure which we are going to calculate. But the analogy cannot be pushed further for numerical calculation.

The change in energy density corresponding to the change of A into A' is given by

$$\frac{E_\lambda'}{E_\lambda} = \left(\frac{c+v}{c-v}\right)^2,$$

[1] Dr. Green, Phil. Mag., June, 1920.

i.e., the energy in the reflected train corresponding to the wave-length λ is therefore increased in the ratio of $[(c+v)/(c-v)]^2$.

An incident pulse of length $(c+v)$ is changed by reflection into a pulse of length of $(c-v)$, on account of motion of the reflecting surface. Hence the increase in energy density per second is

$$E_\lambda\left(\frac{c+v}{c-v}\right)^2(c-v) - E_\lambda(c+v) = E_\lambda(c+v)\left[\frac{c+v}{c-v} - 1\right].$$

This energy is supplied by the work done in advancing the reflecting surface a distance v per second against a pressure p so that

$$pv = E_\lambda(c+v)\left[\frac{c+v}{c-v} - 1\right];$$

$$\therefore \quad p = 2E_\lambda\left(\frac{c+v}{c-v}\right),$$

which is in accordance with the results of Larmor and Edser.

Equation (5) shows that p varies with E_λ, since c and v are constants. It also shows that the pressure on the reflector is maximum for the wave-length for which the energy density is maximum, and will be less than this maximum value for different values of the wave-length as shown in the following table:

T = 2000° abs. carbon glow lamp,

$C/I = 2.8 \times 10^{-2}$ dynes per sq. cm.

$\lambda \times 10^{-4}$ Cm.	Pressure $\times 10^{-4}$ Dynes per Sq. Cm.
8.3	.32
4.8	.64
2.7	.90
1.8	.71
1.2	.32

The total pressure due to whole pulse, consisting of different wave-lengths is given by

$$P = \int_0^\infty 2E\lambda\left(\frac{c+v}{c-v}\right)d\lambda = \frac{2I}{c}\left(\frac{c+v}{c-v}\right), \tag{6}$$

where I is the intensity of total radiation of the incident beam. In the case of stationary reflector, the pressure is given by twice the energy density in the beam, in agreement with Larmor. Equation (6) shows that the pressure is infinite when the reflector is moving with a velocity equal to that of light; in that case the reflector piles up the radiation

as it advances with the velocity of radiation—which of course no one would deny. In the case when it moves away from the radiation with an equal velocity the pressure is zero, since it just keeps ahead and there is no reflection.[1]

The total energy density in front of the reflector corresponding to the wave-length λ is given by E

$$E = E_\lambda + E_\lambda \left(\frac{c+v}{c-v}\right)^2;$$

$\therefore \quad p = kE$, where

$$k = \frac{c^2 - v^2}{c^2 + v^2},$$

which reduces to unity if we neglect second order terms in v/c.

EWING CHRISTIAN COLLEGE,
ALLAHABAD,
Dec., 1920.

[1] Larmor, loc. cit.

THE IONIZATION POTENTIAL OF SELENIUM VAPOR.

BY A. D. UDDEN.

SYNOPSIS.

Ionization potential of selenium vapor was determined from current potential curves obtained with a four electrode, pyrex glass tube. Nickel was used for the electrodes. After the cleaning out process the selenium was spilled into the bottom of the tube and vaporized by means of an oil bath kept at 168 to 282° C. Both total negative current measurements were made and positive current measurements according to the Lenard method, and corrections were applied for the potential fall along the electrically heated salted platinum cathode and for the initial energy of the electrons. The ionization potential comes out 12.7 ± 0.4 volts. Putting this value in the quantum equation we get 980 Å as the short wave-length limit of the selenium spectrum.

THE ionization and resonance potentials of several elements belonging to group VI. of the periodic table have already been determined.[1] In continuation of the study of the elements of this group, this paper presents the results of a determination of the ionization potential of selenium vapor.

The significance of critical potential determinations has frequently been pointed out. When an electron possesses a certain critical speed it is capable of ionizing a given vapor atom by collision. That potential which can impart this speed to an electron is known as the ionization potential of the given vapor. According to Bohr's theory, if the ionization potential V of a vapor has been determined, the limiting frequency ν of the spectrum of this vapor may then be calculated from Planck's formula, $\nu = Ve/h$.

The ionization potential of selenium vapor was obtained by the usual method of accelerating the electrons from a hot filament to metal electrodes to which suitable potentials were applied. Current potential curves were plotted and the ionizing potential was indicated by an abrupt change of curvature in each of the graphs. Corrections were applied for the drop in potential along the filament and for initial velocity of emission of the electrons. The initial velocity correction was made by applying back potentials on the grid just sufficient to stop the electron current.

A diagram of the apparatus used in the present investigation is shown in Fig. 1. The pyrex glass tube was made in two sections, ground to a

[1] Scientific Papers of the Bureau of Standards, No. 400.

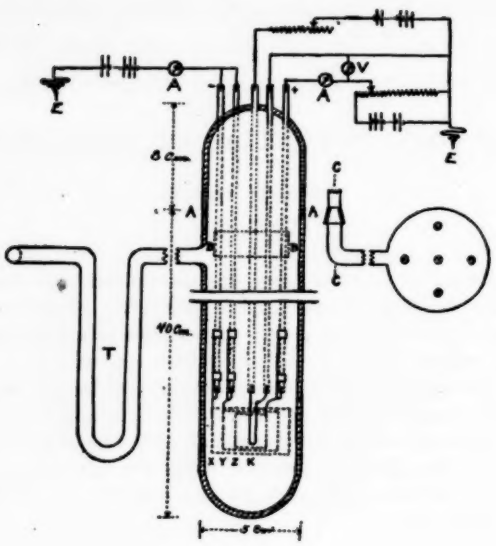

Fig. 1.

smooth fit at *A–A*, and these were sealed together with DeKhotinsky cement. The nickel plate *X* and the grids *Y* and *Z* were cylindrical in shape and placed coaxially with reference to the cathode *K*. The electrodes were held in place by means of clasps fitting on slender pyrex tubes sealed into the upper section of the large tube. A small mica cup at *B–B* contained the selenium which was to be vaporized. The cathode consisted of a thin strip of platinum coated with several applications of barium and strontium oxides. When measurements were being made a freezing mixture of carbon dioxide snow surrounded the trap *T*.

With proper heat treatment of the tube and the electrodes a vacuum of about .003 millimeter pressure was obtained, after which the selenium was spilled into the bottom of the tube by rotating the latter about a horizontal axis *C–C*. The selenium was then vaporized by means of an oil bath surrounding the lower part of the tube. Some difficulty was experienced in finding a metal suitable for use as electrodes in the vapor. Copper was attacked by the vapor and a polarizing layer appeared to form on the surface of iron. A white powder formed on the nickel electrodes but this did not seriously interfere with the flow of electron currents.

The ionization potential was determined by both total current and positive current measurements. In the case of total current measurements, the plate and two grids were connected together so as to form a single electrode to which positive accelerating potentials were applied.

For the positive current or Lenard method the electrodes were connected as shown in the diagram. In the latter case a negative potential of about 15 volts was applied to the outer electrode.

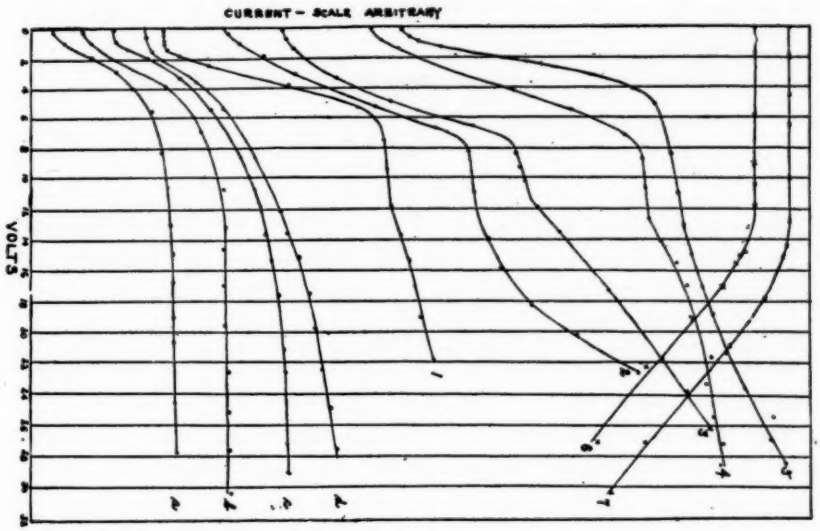

Fig. 2.

Runs were first made without the selenium vapor, keeping the conditions otherwise the same as when the vapor was present in the tube. Curves such as *a*, *b*, *c* and *d* (Fig. 2) were then obtained. It will be noticed that these curves flat off quite regularly and do not show any sudden increase in the electron current. Curves 1, 2, 3, 4, 5, 6 and 7 were made with vaporized selenium present in the tube, the temperature of the vapor varying from 168 to 282 degrees Centigrade for the different runs. Graphs 1 to 5 are total current measurements while 6 and 7 were obtained by the Lenard method. The graphs as plotted include the corrections for potential drop along the filament, the corrections varying from 1.0 to 2.4 volts. The initial velocity corrections are shown in the accompanying table. In some cases the temperature of the filament was so low that no appreciable initial velocity was obtained.

No. of Curve.	Break, Volts.	Initial Velocity, Volts.	Ionization Potential, Volts.	Deviation from Mean.
1	12.0	—	12.0	−.7
2	11.8	1.5	13.3	+.6
3	11.6	.5	12.1	−.6
4	12.7	.1	12.8	+.1
5	13.0	—	13.0	+.3
6	12.5	.1	12.6	−.1
7	13.0	—	13.0	+.3

The average ionization potential of selenium vapor calculated from these measurements is 12.7 ± .4 volts. This is quite close to the value obtained for sulphur by Mohler and Foote.[1] The ionization and resonance potentials for elements belonging to group VI. so far determined are given below.

Element.	Ionization Potential.	Resonance Potential.
Oxygen	155. ± .5	7.91 ± .1
Sulphur	12.2 ± .5	4.78 ± .5
Selenium	12.7 ± .4	——

If the potential 12.7 volts is substituted for V in the expression, $\nu = Ve/h$ the limiting frequency of the spectrum of selenium vapor is seen to be about 980 Ångstrom units. Inasmuch as measurements do not appear to have been made in this region of the selenium spectrum this result can not be confirmed. No arc was at any time visible in the selenium vapor up to thirty volts, the highest potential employed.

It was also desired to measure the resonance potential of selenium vapor. For this purpose, following the work of Mohler and Foote, a second grid was brought into use according to their method. At present it has not been possible to obtain any indication of a resonance potential. With further modifications of the dimensions and distances separating the electrodes it is possible that a resonance potential may be determined. This might provide a more satisfactory correction for the initial velocity of emission of the electrons.

The writer is under obligations to Dr. C. B. Bazzoni for suggestions and advice received during the course of the work upon this experiment

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ON TALBOT'S BANDS AND THE THEORY OF THE LUMMER-GEHRCKE INTERFEROMETER.

By Nihal Karan Sethi.

Synopsis.

New Simple Method of Observing Talbot's Bands.—If a thin strip of *cover glass is immersed in a dispersive medium*, such as a suitable mixture of CS_2 and benzene, with a refractive index such that the group velocity in it is less than in the plate, and if a vertical slit illuminated with white light is observed through the glass strip held in a vertical plane very oblique to the plane of the incident light, two out of the four spectra formed by the edges of the plate exhibit Talbot's bands. The *theory* of the formation of the bands in this way is closely similar to that of the Lummer-Gehrcke plate, and as in the latter, the maxima are narrow and the minima crossed by secondary maxima when the number of internal reflections is small. The appearance, too, is not affected by opening the slit wide.

Interference Bands Analogous to Those given by a Fabry-Perot etalon were also observed with the same simple arrangement. The appearance and behavior of these bands are *described and explained.*

ATTENTION has been drawn by Prof. R. W. Wood[1] to the relation between the theory of Michelson's echelon grating and of the well-known bands in the spectrum discovered by Talbot which are observed on covering half the aperture of the beam in a spectroscope by a thin plate of mica or glass. Wood has pointed out that Talbot's plate is in effect an echelon grating of two elements and has published photographs of Talbot's bands obtained by using a mica echelon of two or more elements as the retarding plate. In the present note, the writer wishes to describe a new and extremely simple method of observing Talbot's bands, which is of interest as it suggests an analogy between these bands and the theory of the Lummer-Gehrcke interferometer.

A thin strip of glass conveniently obtained by cutting from a microscope cover-slip is immersed in a mixture of carbon disulphide and benzene in adjustable proportions. The liquid is contained in a flat cell and means are provided to enable the observer to turn the slip of glass round a vertical axis while its edges are always maintained in a vertical position. On turning the strip so that white light from a distant slit is incident very obliquely on it, an eye placed close to the strip is able to see a pair of spectra on either side of the source of light and another pair on either side of its reflected image. When the inclination of the glass

[1] Phil. Mag., Nov., 1909, p. 758.

strip and the refractive index of the liquid mixture are suitably adjusted, one of either pair of the spectra is seen to exhibit Talbot's bands, while the remaining two show some curious curved fringes. We shall first deal with the former case.

Fig. 1 shows the main features of the arrangement. The edge A of the glass strip acts as a prism and a ray OP is deviated in the direction QR in which the usual spectrum is observed. But owing to the very oblique incidence of light, a number of internal reflections take place and we have a corresponding number of parallel emergent rays $Q'R'$, $Q''R''$, etc., the mutual interference of which is undoubtedly the cause of the Talbot's bands observed in this spectrum. The rays ST, $S'T'$, $S''T''$, etc., give another spectrum similarly crossed by Talbot's bands. These multiple reflections can be easily observed by removing the eye to a distance or by means of a small magnifying lens.

Figs. 2 and 3 (in the plate) are photographs of Talbot's bands observed in this manner. It should be observed that in addition to the very bright principal maxima, the photographs also show feebler secondary maxima in the spectrum—one in Fig. 2 and two in Fig. 3.

That these bands represent a more general case of Talbot's bands is abundantly clear when we remember that the well-known Talbot's bands are caused by the redistribution by a prism of the diffraction pattern due to two adjacent narrow parallel beams which are caused to differ in phase by the introduction of a thin retarding plate in the path of one of them. In the present case we have not two but several such beams differing in phase by regularly increasing amounts, although no thin plates are expressly introduced for this purpose. The prism which re-distributes the diffraction pattern is also included in the glass strip, so that we have a considerable simplification of apparatus.

It is a noteworthy fact that in this experiment, the fringes are observable in the spectrum both when the refractive index μ of glass is smaller than μ' of the liquid mixture, and to some extent also when $\mu > \mu'$. The essential condition is that the group-velocity of light in glass is higher than in the liquid surrounding it. And when by the addition of more benzene, the refractive index of the latter is reduced so much that the group-velocity becomes equal to that in glass for any particular color,[1] these bands disappear in the part of the spectrum lying on the red side of this position. The reason why this is so becomes clear on recalling the condition for the visibility of Talbot's bands, namely, that the light pulses or groups passing through different parts of the dispersing

[1] For a method of ascertaining this see the paper on Powell's Bands by the writer in PHYS. REV., Dec., 1920.

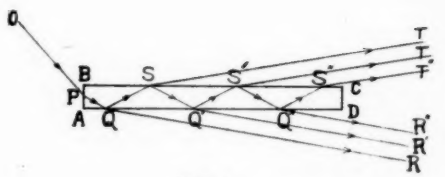
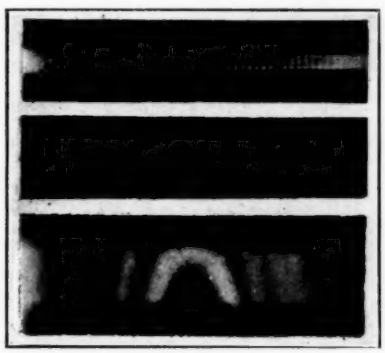


Fig. 1.



Figs. 2, 3, and 5,

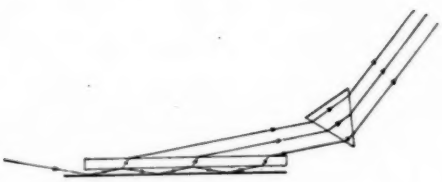


Fig. 4.

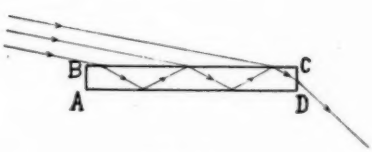


Fig. 6.

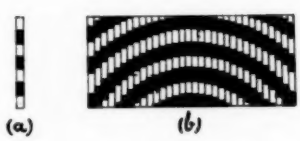


Fig. 7.

NIHAL KARAN SETHI.

prism should be caused to arrive together at the focal plane of the observng telescope. In this case the liquid surrounding the plate has the higher dispersive power and hence the condition cannot be satisfied unless the group-velocity in it is less than within the plate.

In calculating the distribution of light in the resulting spectrum we may follow the treatment of the usual case of Talbot's bands by Rayleigh,[1] and assume in his notation that the successive beams extend from $x = -h$ to $x = -h + d$; $x = -h + 3d$ to $x = -h + 4d$; $x = -h + 6d$ to $x = -h + 7d$, etc., since it can be easily shown that the widths of the beams are all equal being limited by the thickness of the glass strip and that they are separated from each other by intervals equal to the width of any one of them. Remembering that the amplitude of each beam is b^2 times that of its predecessor where b is the coefficient of internal reflection, we shall obtain on integration and addition the value of the intensity I to be given by

$$I = \frac{1}{\xi^2} \sin^2 \frac{\pi \xi d}{\lambda f} \cdot \frac{1}{(1 - b^2)^2 + 4b^2 \sin^2 \frac{\pi}{\lambda}\left(R - \frac{2d\xi}{f}\right)}$$

for the complete set of beams. When the slit is illuminated by white light and the diffraction pattern is spread out into a spectrum we shall have $R = R_0 + \bar{\omega}\xi$. If now $\bar{\omega} = 2d/f$,

$$I = \frac{1}{\xi^2} \sin^2 \frac{\pi \xi d}{\lambda f} \cdot \frac{1}{(1 - b^2)^2 + 4b^2 \sin^2 \frac{\pi R_0}{\lambda}}.$$

The condition for the darkest minima (for they cannot be absolutely dark) is thus seen to be $\bar{\omega} = 2d/f$.

From what has been said above it is clear that in forming these Talbot's bands, the thin glass plate acts in a manner essentially similar to that in which the well-known Lummer-Gehrcke plate acts. This is made still clearer when monochromatic light is employed. The diffraction pattern now observed shows the same sharp and narrow maxima separated by broad dark bands which are themselves crossed by feeble secondary maxima when the number of internal reflections is not very large. As the incidence inside the plate becomes more and more oblique, the bands also gradually increase in width. And lastly the bands remain quite clear even when the slit is widened, so much so that Talbot's bands produced in this way can be easily observed without any slit whatsoever.

That the Lummer-Gehrcke plate does not ordinarily show Talbot's bands when illuminated by white light is due not only to the very large

[1]Ency. Brit., 11th edition, Vol. VIII., p. 250 and Sc. Papers, Vol. III., p. 123.

retardations which it produces and which will require the dispersing apparatus to have an exceedingly large resolving power,[1] but also to the more important fact that its dispersion takes place in the wrong direction. This becomes the clearer when we consider the small correction, first pointed out by Baeyer,[2] in calculating the separation of two close wave-lengths λ and $\lambda + d\lambda$ observed with the Lummer–Gehrcke plate. The angular distance between the maxima of these wave-lengths can be easily shown to be

$$d\theta = -\frac{1}{\sin\gamma\cos\theta}\left\{\frac{n\cos\gamma}{2t} - \frac{d\mu}{d\lambda}\right\} d\lambda,$$

where t is the thickness of the plate, γ and θ are the angles of internal incidence in and of emergence from the plate and n represents the order of the maxima and is equal to $(2\mu t\cos\gamma)/\lambda$. This expression for the separation consists of two terms, one due to the change in the retardation consequent on a change in λ and the other due to the dispersion of the plate. Putting

$$\mu = 1.5, \quad \frac{d\mu}{d\lambda} = -\frac{2B}{\lambda^3}, \quad B = .5 \times 10^{-10}, \quad \lambda = 5 \times 10^{-5}$$

and taking the emergence to be almost grazing, so that

$$\sin\gamma = \frac{1}{\mu} = \frac{2}{3} \quad \text{and} \quad \cos^2\gamma = \frac{5}{9},$$

we get

$$\frac{n\cos\gamma}{2t} = \frac{\mu\cos^2\gamma}{\lambda} = 1.5 \times 10^4,$$

and

$$\frac{d\mu}{d\lambda} = -\frac{2B}{\lambda^3} = -.08 \times 10^4.$$

But if the plate is surrounded by a medium whose refractive index μ does not differ much from that of the plate itself and whose dispersion is *greater*, these two terms become comparable and since the sign of the second is reversed, it is possible under favorable conditions to have the effect of the first term completely destroyed by the second; in other words, to have the maxima remaining fixed while the wave-length is altered. In the case of a mixture of carbon disulphide and benzene adjusted till μ' differs from μ by .01, the value of $\cos^2\gamma = 1 - 1/(1.01)^2 = .02$ nearly; so that the first term in the above expression becomes

[1] See T. E. Doubt, PHYS. REV., Oct., 1917, p. 322.

[2] Verh. der Deutsch. Phys. Ges., 10, 1908, p. 733.

.06 × 10⁴ nearly. And the resultant dispersion $d/d\lambda(\mu - \mu')$ is about three fourths of the dispersion of glass, so that the second term also is equal to about .06 × 10⁴.

It may also be mentioned that Talbot's bands can also be observed with the interference plate recommended by Barnes.[1] The arrangement is shown in Fig. 4.

The thin plate of air is formed between two interferometer plates one of which is heavily silvered in front. A separate prism is used to produce the spectrum. In the position of the prism shown in the figure, the Talbot's bands with the subsidiary maxima described in the previous case are obtained, but when the prism is turned round so as to receive the retarded beams on the thicker side, no bands are produced.

Although not connected with the subject of Talbot's bands the writer must take this opportunity of describing a phenomenon which one cannot fail to notice while observing these bands with the arrangement of Fig. 1. It has already been mentioned that in addition to two spectra showing Talbot's bands and formed by the edge *A* of the plate, two other spectra are also observed. They are found to be due to the edges *C* and *D* of the plate and in general within certain limits of adjustment of the refractive index of the liquid, each of them exhibits in some part of it a series of curved dark bands (Fig. 5 in the plate) which drift up or down and give place to new ones in the centre somewhat in the same way as the rings in a Fabry-Perot etalon while the center itself slowly shifts across the spectrum when the glass strip is slowly turned round. The curvature of these arcs is found to depend on the inclination of the edges *C* and *D* to the slit which is the source of light. When they are carefully adjusted to be strictly parallel, we have a series of vertical bands on either side of a rather broad central patch and these become narrower and fainter as the distance from the central patch increases until they disappear altogether. Rotation of the glass strip makes them close in or spread out exactly like the curved bands described above. But the slightest inclination of the edge *C* to the slit makes them curved and the sign of the curvature may be altered by an inclination in the opposite direction. When the inclination is very considerable, they appear as horizontal arcs of circles of very large radii.

The disposition of the rays which cause this phenomenon is shown for one of the spectra in Fig. 6. A number of parallel rays incident on the face *BC* come out of *CD* after multiple internal reflections as a system of coincident beams, the components of which differ in phase by regularly increasing amounts. That these are the cause of the curved bands is

[1] Astrophys. Journal, 19, 1904, p. 200.

seen from the fact that they disappear when the beams are cut off by a screen. Such a system will no doubt produce the usual Fabry-Perot rings, but on account of the very small retardations produced by the plate, the whole of the slit will be covered by the central ring only. A spectrum in which each monochromatic element consists of such a pattern cannot be expected to show any bands. But there is one circumstance which considerably alters the situation. The retardation in phase which is easily seen to be $(2\mu t \cos \gamma)/\lambda$ does not continually increase from one end of the spectrum to the other, but becomes stationary at a certain point and then begins to decrease. The condition for its becoming stationary is evidently

$$\frac{d}{d\lambda}\left(\frac{2\mu t \cos \gamma}{\lambda}\right) = 0.$$

This combined with the condition $\mu \sin \gamma = \mu' \sin i$ will give

$$\tan^2 \gamma = \frac{\frac{1}{\mu}\frac{d\mu}{d\lambda} - \frac{1}{\lambda}}{\frac{1}{\mu'}\frac{d\mu'}{d\lambda} - \frac{1}{\mu}\frac{d\mu}{d\lambda}}.$$

Putting roughly

$$\mu = \mu' = 1.5, \frac{d\mu}{d\lambda} = -1 \times 10^3, \frac{d\mu'}{d\lambda} = -1.5 \times 10^3 \text{ and } \lambda = 5 \times 10^{-5} \text{ cm.},$$

we obtain $\gamma = 81°$ nearly, which not only proves the possibility of this condition being fulfilled but is moreover of the right order of magnitude.

In the neighborhood of the wave-length for which this condition is satisfied, the phase change is very slow and the condition of maximum or minimum intensity persists for a number of neighboring wave-lengths. The spectrum in this neighborhood will therefore appear to be crossed by vertical dark bands which will gradually become narrower on either side of this point.

Another fact confirmed by observation is that this point of stationary retardation is shifted towards the red end of the spectrum when the angle of incidence is increased, because the denominator in the formula for tan γ decreases faster than the numerator when λ is increased.

The above discussion refers to the case when the slit is strictly parallel to the edge of the glass strip. When, however, any one of them is slightly turned about the line of sight, there is another factor which gives rise to the curved bands. The light from all the points of the slit is not now incident on the strip at the same angle, so that the interfering beams

due to different parts of the slit have different retardations and therefore the image of the slit in monochromatic light becomes crossed by dark bands; and the more is the tilt increased, the greater is the number of these bands. An easy numerical calculation shows that a very small change in the angle of incidence is enough to change the retardation by π. Since the retardation

$$\rho = \frac{2\mu t \cos \gamma}{\lambda},$$

$$\frac{d\rho}{d\gamma} = -\frac{2\mu t \sin \gamma}{\lambda}.$$

Putting

$\mu = 1.5$, $t = .025$ cm., $\lambda = 5 \times 10^{-5}$ cm. and $\sin \gamma = 1$ nearly, $\frac{d\rho}{d\gamma} = 1.5 \times 10^{3}$

therefore, the change in γ required for a change of π in the value of ρ is

$$\frac{\pi}{1.5 \times 10^{3}}.$$

The result, then, of this inclination of the slit is that the image of the slit appears broken up as in Fig. 7, *a*. The disposition of the dark and bright portions will vary with the wave-length of the light used. With a monochromator as the source of illumination, one can watch the slow shift of these upwards or downwards as the wave-length is continually altered, till the constancy of retardation with change of λ is reached and then they begin to march in the reverse direction. Illuminated with white light, these various images must be distributed in the spectrum much as in Fig. 7, *b* and will give rise to the curved bands referred to above. Inclining the slit in the opposite direction produces the curves with the concavity turned upwards.

The experimental work was done in the laboratory of the Indian Association for the Cultivation of Science, Calcutta, and the writer's best thanks are due to Prof. C. V. Raman for his unfailing interest in the work.

210 Bowbazaar Street,
Calcutta, India,
15th March, 1921.

THE REFLEXION OF X-RAYS BY CRYSTALS.

BY H. A. WILSON.

SYNOPSIS.

Theory of Reflection of X-rays from a Point Source, by a Perfect Crystal.—The derivation of the expression for the total reflected energy as obtained by other physicists, is given in simpler form. It is shown that the reflected rays are parallel in the plane of incidence but diverge in the perpendicular plane. Making the simplifying assumption that no ray is reflected more than once from any plane of atoms and that the absorption by the crystal is negligible, expressions for the intensity at any point in the reflected beam are derived. It is shown that interference fringes are to be expected whose distance apart under ordinary circumstances may be of the order of 4×10^{-4} cm. The error due to the above mentioned simplifying assumptions can be corrected by multiplying by the appropriate exponential factor.

THE theory of the reflexion of x-rays by crystals has been discussed by W. H. Bragg,[1] C. G. Darwin,[2] A. H. Compton[3] and W. L. Bragg.[4] The last three of these investigators obtained equivalent results for the total energy reflected.

The main object of the present paper is to give the theory of the reflexion of homogeneous x-rays, coming from a point source, by a perfect crystal, in a simpler form than has hitherto been done. The results obtained agree with those of the previous investigators but some points of detail with regard to the character of the reflected beam are brought out clearly by the new method of calculation.

The very interesting results recently described by Bergen Davis[5] seem to show that in some cases reflexion takes place as though the crystal were nearly perfect.

If an electron with charge e and mass m is exposed to a beam of plane polarized x-rays in which the amplitude of the electric intensity at the electron is A, then the amplitude A' in the scattered radiation in the plane perpendicular to the electric intensity is given by

$$A' = Ae^2/rmc^2,$$

where c denotes the velocity of light and r is the distance from the electron.

[1] W. H. Bragg, Phil. Mag., May, 1914.
[2] C. G. Darwin, Phil. Mag., Feb. and April, 1914.
[3] A. H. Compton, PHYS. REV., Jan., 1917.
[4] W. L. Bragg, R. W. James and C. H. Bosanquet, Phil. Mag., March, 1921.
[5] Bergen Davis and W. M. Stempel, PHYS. REV., May, 1921.

If instead of an electron we have an atom containing N electrons then, following W. L. Bragg, we may write

$$A' = AFe^2/rmc^2,$$

where F is a function of the angle between the incident and scattered radiation which should approach N as the angle approaches π.

Consider first the reflexion by a single layer of atoms containing n atoms per unit area. Let the incident radiation come from a point source S (Fig. 1), and let it be plane polarized with the electric intensity perpendicular to the plane of incidence. Consider the reflected amplitude at any point I. The reflected rays at I will have gone along the path SPI such that the angles SPA and IPB are equal. The area of the first Fresnel zone on the surface AB of the crystal can be easily shown to be $\pi\lambda r_1 r_2/(r_1 + r_2) \sin\theta$ where $r_1 = SP$, $r_2 = PI$, θ is the angle SPA and λ the wave-length of the incident radiation.

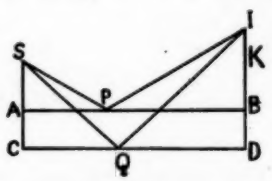


Fig. 1.

Let the amplitude in the incident spherical waves at P be a/r_1, then the amplitude at I of the reflected radiation is

$$\frac{1}{2}\,\frac{2}{\pi}\,\frac{n\pi\lambda}{\sin\theta}\,\frac{r_1 r_2}{r_1 + r_2}\,\frac{a}{r_1}\,\frac{F}{r_2}\,\frac{e^2}{mc^2} = \frac{n\lambda aFe^2}{(r_1 + r_2)\sin\theta \cdot mc^2}.$$

This is inversely as $r_1 + r_2$ as it should be, for the reflected rays appear to come from the image of S formed by the plane AB.

Suppose now that we have a series of similar layers of atoms equally spaced below AB. The vibration at I will be the resultant of the vibrations due to all the layers. Let d denote the distance between successive layers. Successive reflexions up and down will cause a single incident ray to emerge as a series of parallel rays. The calculation will be made now on the simple assumption that successive reflexions up and down can be neglected so that each plane reflects only once. It will also be assumed that the reflected rays from each plane have the same intensity although of course owing to absorption and reflexions the intensity must diminish with the depth of the planes below the surface of the crystal. The effect of these assumptions on the results obtained will be considered later.

Consider the vibration at I due to a layer CD at a distance pd below AB so that p is an integer. Let $SA = h_1$, $IB = h_2$, $AP = k_1$, $PB = k_2$ then the path SQI of rays reflected by the layer CD is longer than the path SPI by

$$\sqrt{k^2 + (h + 2pd)^2} - \sqrt{k^2 + h^2},$$

where $k = k_1 + k_2$ and $h = h_1 + h_2$ for the angles SQC and IQD are equal.

Now suppose the angle SPA or θ satisfies the equation $\lambda = 2d \sin\theta = 2dh/r$ then the difference between the paths SQI and SPI will be nearly but not exactly equal to $2pdh/r$. Let this difference be equal to $(2pdh/r) + N\lambda$ where N is a number which is small unless p is large. Then we have

$$\sqrt{k^2 + (h + 2pd)^2} - \sqrt{k^2 + h^2} = \frac{2\,pdh}{r} + N\lambda,$$

so that

$$4p^2d^2\left(1 - \frac{h^2}{r^2}\right) = 2rN\lambda + N^2\lambda^2 + 2pN\lambda^2.$$

The terms $N^2\lambda^2$ and $2pN\lambda^2$ are quite negligible compared with $2rN\lambda$ so that since $h/r = \sin\theta$,

$$4p^2d^2\cos^2\theta = 2rN\lambda,$$

or

$$p = \frac{1}{d\cos\theta}\sqrt{\frac{rN\lambda}{2}}.$$

In calculating the resultant vibration at I path differences equal to a multiple of λ may be neglected so that the vibration at I due to the layers for which p is between p and $p + \delta p$ may be taken equal to

$$\frac{an\lambda Fe^2}{rmc^2\sin\theta}\cos\frac{2\pi}{\lambda}(ct - N\lambda)\delta p,$$

since the change in N when p is increased by unity is clearly very small. Hence the resultant vibration at I is

$$\frac{an\lambda Fe^2}{rmc^2\sin\theta}\int_0^\infty \cos\frac{2\pi}{\lambda}(ct - N\lambda)\delta p$$

$$= \frac{an\lambda Fe^2}{rmc^2\sin\theta}\int_0^\infty \left[\cos 2\pi N\cos\frac{2\pi}{\lambda}ct + \sin 2\pi N\sin\frac{2\pi}{\lambda}ct\right]\delta p.$$

Substituting for p in terms of N and putting $N = x^2/4$ we get for the amplitude at I

$$\frac{an\lambda Fe^2}{rmc^2\sin\theta}\frac{1}{d\cos\theta}\sqrt{\frac{r\lambda}{2}}\frac{1}{2}\left\{\left[\int_0^\infty \cos\frac{\pi x^2}{2}\,dx\right]^2 + \left[\int_0^\infty \sin\frac{\pi x^2}{2}\,dx\right]^2\right\}^{1/2}$$

$$= \frac{an\lambda Fe^2\sqrt{r\lambda}}{4rmc^2\sin\theta\cdot d\cos\theta} = \frac{an\lambda^{1/2}Fe^2}{2mc^2r^{1/2}\cos\theta}.$$

Thus it appears that the amplitude at I varies inversely as the square root of the length of the path from the point source. This shows that the reflected rays at I form a parallel beam in the plane of incidence. This is clear also from elementary considerations for it is only when θ is extremely close to the value given by $\lambda = 2d \sin \theta$ that there is appreciable reflexion from a series of planes so that the reflected rays must proceed as in Fig. 2. The reflected rays are parallel in the plane of incidence but diverge in the perpendicular plane so that the amplitude varies as $r^{-1/2}$ and the intensity as r^{-1}.

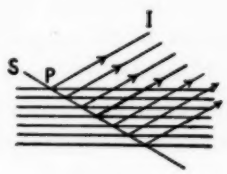


Fig. 2.

The intensity at I is due to rays which have passed through only a very small thickness of the crystal so that the result obtained for the amplitude at I will be approximately correct in spite of the simplifying assumptions made that each plane reflects only once and that the amount reflected from each plane is the same.

Consider now the amplitude at K (Fig. 1) on the perpendicular from I to the crystal surface. Denote IK by z. The amplitude at K, if the same simplifying assumptions are made, will be double that at I provided IK is big enough for K to be outside the diffraction fringes at the upper surface of the reflected beam. For at K in this case we get reflected beams from each layer of atoms for which p varies practically from $-\infty$ to $+\infty$ instead of from 0 to ∞ as at I. The distribution of intensity along IK will be the same as that in the shadow of a straight edge so that the reflected energy may be calculated by assuming the intensity to be constant along IK below I and zero above I and then allowing for absorption and the effect of successive reflexions. The radiation at K is reflected in the crystal at a depth $\frac{1}{2}IK$ below the surface so that it has passed through a thickness $IK/\sin\theta$.

It is easy to see that the intensity at K will fall off as z increases approximately exponentially even when all the possible reflexions up and down are taken into account. The effect of reflexions will be to cause the intensity at K to fall off less slowly as z increases than it falls off on the assumption that each plane reflects only once. We may therefore suppose that the intensity is proportional to $\epsilon^{-\mu z/\sin\theta}$ where μ is the apparent coefficient of absorption giving the diminution of intensity due to true absorption and to reflexions from the planes. Hence the total energy reflected per unit time in a length w perpendicular to the plane of incidence is

$$c \cos\theta \cdot w \left(\frac{an\lambda^{1/2}Fe^2}{mc^2r^{1/2}\cos\theta}\right)^2 \int_0^\infty \epsilon^{-\mu z/\sin\theta} dz = \frac{wa^2n^2\lambda F^2e^4 \sin\theta}{\mu m^2c^3 \cos\theta \cdot r},$$

since the energy flow is parallel to PI and so equal to $c \cos\theta$ times the square of the amplitude per unit area of the plane IK.

Consider the energy reflected between two planes meeting on the perpendicular from S to the surface of the crystal having an angle ϕ between them so that $w = \phi r \cos\theta$ and the reflected energy E_r is given by

$$E_r = \frac{a^2n^2\lambda F^2e^4\phi \sin\theta}{m^2c^3\mu},$$

which is independent of r, as it should be. If we put $\mu = 0$ then E_r becomes infinite. This is because the vertical width of the reflected beam becomes infinite. The intensity at any point remains finite.

Now consider the incident energy in the angle ϕ and between glancing angles θ_1 and θ_2 such that $\theta_1 > \theta > \theta_2$ and let $\theta_1 - \theta_2 = \psi$. The incident energy per unit time is then

$$E_i = c\frac{a^2}{r^2} r \cos\theta \cdot \phi \cdot r\psi,$$
$$= ca^2\psi\phi \cos\theta.$$

Hence

$$\frac{E_r}{E_i} = \frac{n^2\lambda F^2e^4 \sin\theta}{m^2c^4\mu\psi \cos\theta}.$$

Let N denote the number of atoms per unit volume so that $n = Nd$ which with $\lambda = 2d \sin\theta$ gives

$$\psi\frac{E_r}{E_i} = \frac{N^2\lambda^3F^2e^4}{2m^2c^4\mu \sin 2\theta}.$$

When this is multiplied by the polarization factor $\frac{1}{2}(1 + \cos^2 2\theta)$ and the Debye temperature factor $\epsilon^{-B\sin^2\theta}$ it agrees with the results obtained by Darwin, A. H. Compton and W. L. Bragg. Darwin and W. L. Bragg got it for an imperfect crystal only. In the case of a perfect crystal it appears that μ should be greater than the true absorption coefficient.

So far only the intensity at I and at K when K is not very near to I have been calculated. It is easy to calculate the intensity for any position of K if we make the same simplifying assumptions as before. The plane which reflects to K exactly at the angle θ is at a depth $z/2$ below the surface of the crystal and the length of the path from S to K of the ray reflected from this plane is the same for all values of z. The

quantity p may therefore be taken to vary from 0 to ∞ for the part of the crystal below this plane and from 0 to $-z/2d$ for the part above it. The vibration at K is therefore, when the diminution of intensity due to absorption and reflexion is neglected

$$\frac{an\lambda Fe^2}{rmc^2 \sin\theta}\int_{-z/2d}^{\infty} \cos\frac{2\pi}{\lambda}(et - N\lambda)\delta p,$$

so that the amplitude at K is equal to

$$\frac{an\lambda^{1/2}Fe^2}{\sqrt{2}\, mc^2\, r^{1/2}\cos\theta}\left\{\left[\int_{-\beta}^{\infty}\cos\frac{\pi x^2}{2}\,dx\right]^2 + \left[\int_{-\beta}^{\infty}\sin\frac{\pi x^2}{2}\,dx\right]^2\right\}^{1/2},$$

where

$$\beta = z\cos\theta\cdot\sqrt{\frac{2}{r\lambda}}$$

just as in the diffraction fringes near the shadow of a straight edge in parallel light. This agrees with the previous conclusion that the reflected rays form a parallel beam in the plane of incidence.

The greatest intensity occurs almost exactly when $\beta = \sqrt{3/2}$ so that $z\cos\theta = \sqrt{3r\lambda/4}$. If $r = 40$ cm. and $\lambda = 2\times 10^{-8}$ cm. then this gives $z\cos\theta = 8\times 10^{-4}$ cm. The second maximum occurs when $\beta = \sqrt{7/2}$ so that $z\cos\theta = 12\times 10^{-4}$ cm. the distance between the first two maxima is therefore 4×10^{-4} cm., which is big enough to observe with a microscope. If z is greater than say 3×10^{-3} cm. the fluctuations in the amplitude become small and the amplitude may be taken to be twice that at I multiplied, of course, by the absorption factor.

RICE INSTITUTE,
HOUSTON, TEXAS,
May 24, 1921.

THE EFFECT OF THE AGE AND THE CONCENTRATION OF A SOLUTION OF RHODAMINE-B UPON THE PHOTOELECTRIC CURRENT DEVELOPED.

BY RUTH YEATON JENKINS.

SYNOPSIS.

Study of Rhodamine-B Photoactive Electrolytic Cell.—Two identical semi-transparent films of Pt, both sputtered on one piece of glass and baked at 500° C., were used as electrodes of a cell into which various solutions of rhodamine-B in alcohol were successively introduced. For a fresh solution, the photoelectric current developed by illuminating one electrode was found to increase with time to a steady value. The sensitiveness was decreased by exposure to room light, but recovered in the dark. With increasing concentration the sensitiveness increased to a maximum for 3 per cent. and then decreased. The current-time curves obtained with intermittent illumination vary in form with the concentration, showing saturation for low concentrations, reaching maxima for concentrations of 1 to 3 per cent. and increasing indefinitely for higher concentrations. These and other observations show that the phenomenon is quite complicated.

Relative Conductivity of Solutions of Rhodamine-B in Alcohol was measured for concentrations up to 8 per cent.

Effect of a Flowing Electrolyte upon the Potentials of the Electrodes for a Solution of Rhodamine-B in Alcohol.—The Pt electrode against which the electrolyte flowed became negative with respect to the other, the effect being proportional to the rate of flow.

IF one takes a cell consisting of two platinum electrodes in a solution of certain fluorescent substances, such as eosin, fluorescein, rhodamine, etc., and keeps one electrode in the dark, illuminating the other through the solution, or, as has proved more satisfactory, illuminating the solution through a semi-transparent electrode sputtered on the inside of the cell wall, an electromotive force is developed, such that the photoelectric current tends to flow from the illuminated to the dark electrode, in the external circuit.

As a minor part of his investigation of cells of this type, A. Goldmann[1] tried the effect of the concentration of an alcoholic solution of Rhodamine-B upon the current obtained. He started with a saturated solution and repeatedly diluted it to half its previous strength, finding that, with a

[1] A. Goldmann, Lichtelectrische Untersuchung an Farbstoffzellen, Annalen der Physik, Vol. 27, p. 449, 1908.

fixed strength of illumination, the current increased continuously with the concentration.[1]

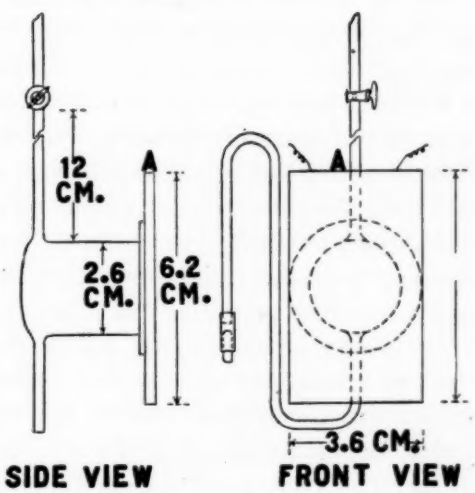
Concentration.....	1	1/2	1/4	1/8	1/16	1/32	1/64
Current.....	100	70	35	10	5	2	0

C. C. Murdock[2] experimenting with a 6 per cent. solution of the same dye, found that his results could be reproduced accurately only as long as he confined the illumination of the cell to relatively short periods of time. The limiting time of illumination for which results could be reproduced was not determined.

As Goldmann also spoke of a "fatigue" effect which caused a decrease in sensitiveness when the solution had been exposed to very intense light, or had been illuminated for a long time, it was thought advisable to repeat that portion of his investigation which dealt with concentration, since it seemed possible that, by the time the lower concentrations were reached, this "fatigue" had reduced the sensitiveness of his solution.

Fig. 1 shows front and side elevations of the cell used. One end of a short piece of one inch glass tubing was closed and small tubes sealed in at the opposite ends of a diameter near this end. One of these tubes contained a stopcock and the other was bent as shown in the front view. They were used for the purpose of filling and emptying the cell. On the other end of the large tube there was blown a flange, the face of which was ground plain and closed with a plate, *A*. This was a piece of plate glass, 6.2 cm. long by 3.6 cm. wide, upon which there had been deposited by cathodic sputtering the semitransparent platinum films shown in Fig. 2. Each film was 6 mm. wide with a resistance of approximately 400 ohms, and the distance between the nearest edges of the two films

FIGURE 1

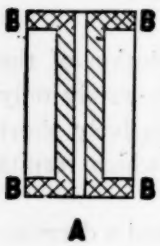


[1] Goldmann (p. 476) gave the following table, in which 1 represented a saturated solution and 100 the current obtained from it. Other concentrations and currents were given in terms of these arbitrary values.

[2] C. C. Murdock, A Study of the Photo-active Electrolytic Cell, Platinum—Rhodamine-B —Platinum, PHYS. REV., Vol. XVII., p. 626, 1921.

was 4 mm. Both films were sputtered at the same time and were therefore as nearly alike as possible. This and the small distance between them, insured a small "dark current." (The size of the dark current increases with the difference in density and with difference in temperature of the two electrodes.)[1]

FIGURE 2



It was found necessary to bake the films at about 500° C. for several hours. The heavy ends *B*, *B* were then copper-plated and the connecting wires soldered to them, thus insuring a better contact than could be obtained with clamps. The parts of the cell were then cemented together. Du Pont Household Cement, thinned with a little amyl acetate, was found very satisfactory for this purpose. Several preliminary coats were applied to the separate parts of the cell and allowed to dry thoroughly before the two pieces were finally put together. In this way it was found possible to apply the cement over the electrodes without injuring their conductivity.

One of the semitransparent electrodes was screened by black paper and the cell was placed in a light tight box fitted with a shutter. In this way the solution could be illuminated through the other film.

A Leeds and Northrup (No. 2285 High Sensitivity) galvanometer, internal resistance of 295 ohms, critical damping resistance of 150,000 ohms, sensitivity of 10,200 megohms, was so arranged that it was shunted by a little less than its critical damping resistance throughout the experiment. One terminal of the cell was connected directly to one end of the damping resistance; the other, to a movable contact on the damping resistance which permitted the sensitiveness to be varied.

The source of illumination was a 40-watt tungsten lamp, used at a constant voltage and at a constant distance from the cell. Since relative measurements only were desired, however, the transmission of the electrodes, the area exposed to the solution and the intensity of the light falling upon them were not determined. A water cell with glass sides 2.5 mm. thick, inside width of 11 mm. and large enough completely to cover the shutter opening, was put between the lamp and the photoelectric cell to stop any heat radiation from the lamp.[1]

In order to have the previous history of all solutions as nearly alike as possible, Goldmann's method of diluting a concentrated solution was not followed. Instead the 95 per cent. alcohol and the dye were mixed in the desired proportions at a definite time before each solution was to

[1] During the readings on the first solution the water cell was not used and the lamp was at a correspondingly greater distance from the photoelectric cell.

be used (about one and one half days). All solutions were kept in clear glass bottles, exposed to the general light of the room, but not to direct sunlight. Later experiments tend to show that these conditions were not sufficiently uniform for very exact work, inasmuch as there was no way to regulate the light in the room with varying weather conditions. Variations caused by such irregularities would not, however, change the general form of the results.

The solution under observation was placed in the cell and illuminated for intervals increasing by 18 or 27 second steps from 18 seconds to 9 minutes. For the measurement of time, a chronograph drum was arranged so that it sounded a signal once every revolution. The interval between these signals was very constant and approximately equal to 9 seconds. The time between periods of illumination was, at first, only long enough for the galvanometer to return to its undeflected position, about 3 min. for short exposures and 6 min. for longer ones. This interval was later made four times the length of the previous exposure. Galvanometer readings were taken once every 9 seconds for both the growth and the decay of the current developed. Since, however, the decay curves do not have any obvious bearing upon the points taken up in this paper they are not included.[1]

Observations on the most dilute solution were taken first and the cell rinsed with a little 98 per cent. alcohol before the next solution was drawn in. The concentration of each solution was determined at the end of the run. The curves[2] obtained by plotting galvanometer deflections as abscissae against time in revolutions of the chronograph drum as ordinates show several interesting features:

$$1 \text{ cm. deflection} = 1.82 \times 10^{9} \text{ amp.}$$
$$1 \text{ revolution} = 9 \text{ seconds.}$$

1. The photoelectric sensitiveness, instead of increasing steadily with increasing concentration as found by Goldmann, passes through a maximum value at a concentration of about 3 per cent. This is shown in Figs. 3 and 4.[3] To confirm this result and to fix more closely the position of the maximum a second set of solutions was made up and tested. In Fig. 4 the results obtained from the first set of solutions are indicated by $\times$; those from the second by $\odot$.

[1] Representative decay curves for each solution have been filed in the Library at Cornell University.

[2] No attempt was made to indicate the separate points plotted, as, with very few exceptions, the line drawn completely covered them.

[3] In making Fig. 4, the concentration by weight was plotted against the deflection at the end of the first 18 sec. exposure, assuming that the fatigue effects would then be negligible and that the currents would still be proportional to the true sensitiveness of the solutions.

2. Three different forms of curves were obtained. In the first, the photoelectric current increases to a constant value; in the second, it passes through a maximum; in the third, it continues to increase indefinitely. In Fig. 3, *A* and *B* are of the first type, *C* and *D* of the second, and *E* and *F* of the third. The length of time before the current maxi-

FIGURE 3

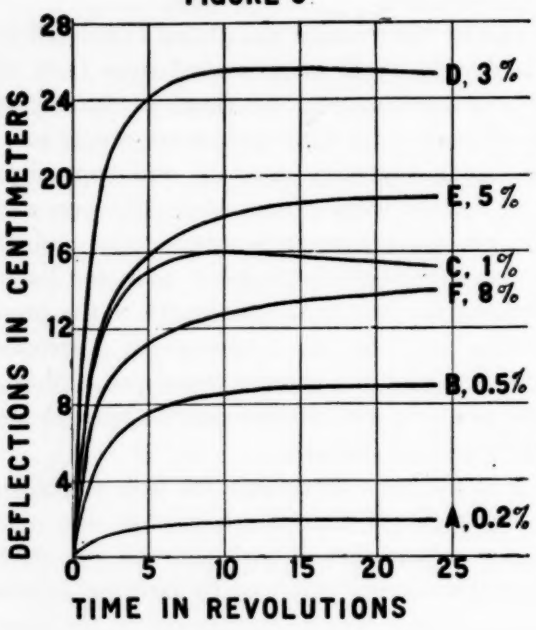
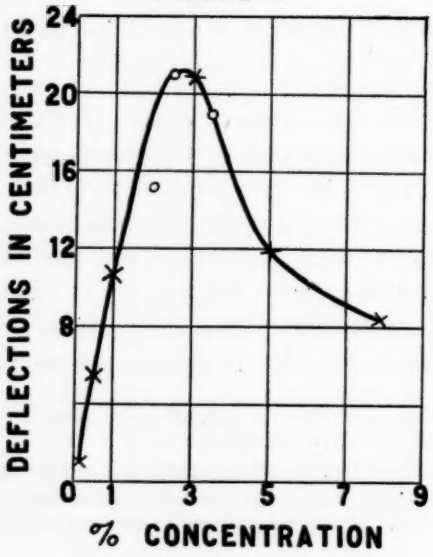


FIGURE 4



mum was reached in the curves of the first and second types varied slowly at first and then very rapidly with the change in concentration. This is shown in Fig. 5. These results are in agreement with those of C. C. Murdock who, working with a 6 per cent. solution, found the current still rising after several hours. Goldmann, on the contrary, says that in all cases the current comes to a steady value with illumination.

The current maximum exhibited by certain concentrations may be caused by a "fatigue" effect, working in opposition to the photoelectric sensitiveness of the solution. This "fatigue" might be thought of as increasing during illumination to a nearly constant value; which value is a function of the concentration of the solution. The time to reach this fairly constant value might also be a function of the concentration, increasing slowly at first and then rapidly with increased concentration. Such an effect would explain the differences in the rapidity with which the current fell, after reaching its maximum, for different solutions and the shift of the position of the current maximum.

FIG. 5

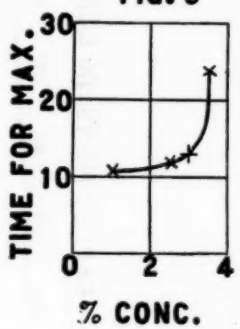
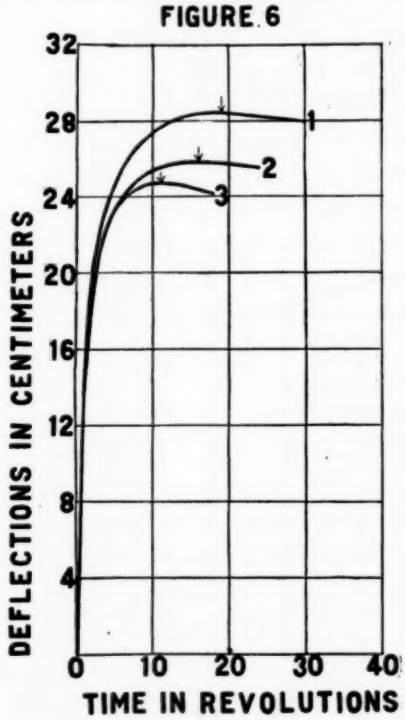


FIGURE 6



3. For a given solution, the current maximum was found to shift toward the left with the length of time the solution had stood "in the light." No such shift was observed for the four days the solution had been standing "in the dark." ("In the light" is defined as:—In a clear glass bottle, exposed to the general light of the room. "In the dark" is defined as:—In the cell on closed circuit and inside the light tight box.) (See Figs. 6 and 7.)

Parts of these same solutions gave the same type of curves after having been kept in bottles in a light tight box for six months and not exposed to the light until they were in the cell and the experimental illumination was begun. The maximum

FIGURE 7

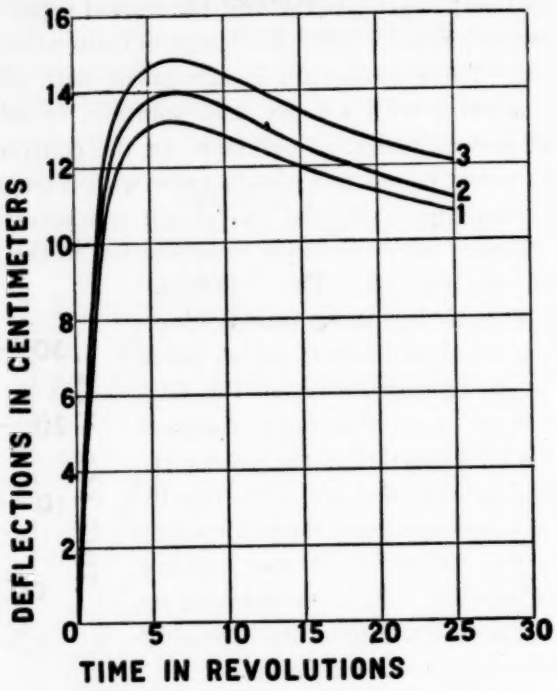
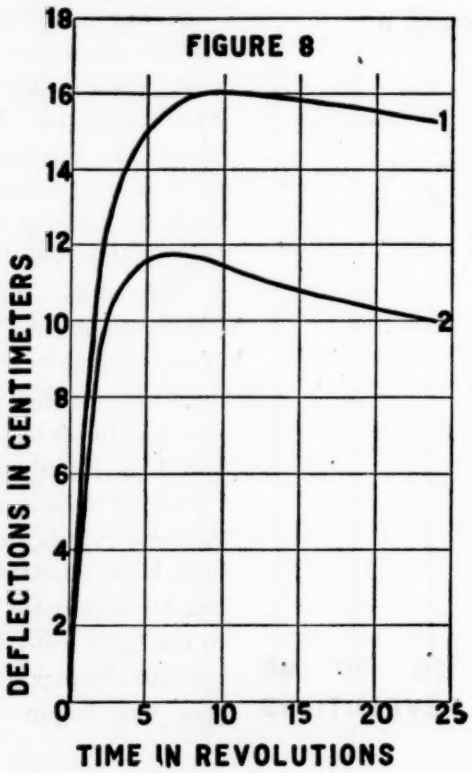


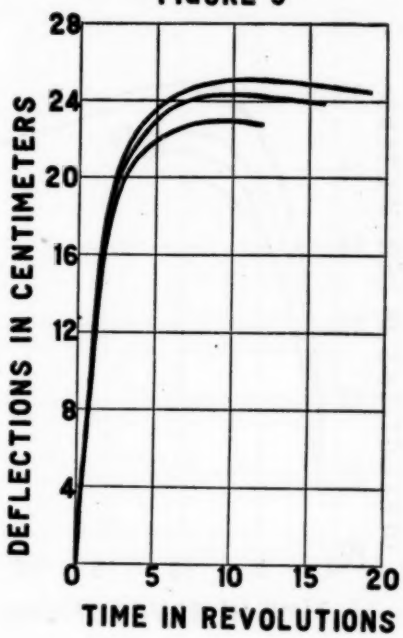
FIGURE 8



had, however, shifted quite far to the right and the sensitiveness of the solutions was only about half its former value.

4. In investigating this point, it was found that there was a marked decrease in the sensitiveness of a solution which had been left standing "in strong light" (Fig. 8) but that a solution which had recently been standing in strong daylight, increased in sensitiveness again when put "in the dark "(Fig. 7) and that this recovery was begun even during the first run made with the solution (Fig. 9). In this figure it is seen that the curves for exposures of less than 2 minutes lie directly upon one another. For longer exposures, there was a fairly steady increase in sensitiveness.

FIGURE 9



A new solution was mixed in the dark, drawn into the cell as soon as it seemed likely that solution was complete (about twenty-four hours) and its sensitiveness studied. It was found that the sensitiveness increased at a gradually decreasing rate for a few days and then reached an approximately steady value.

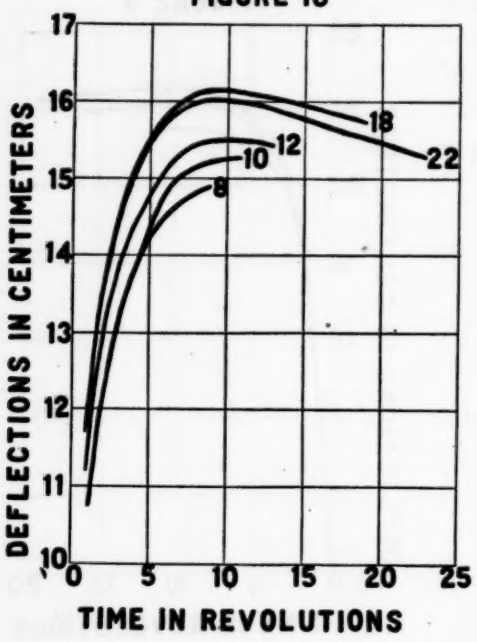
5. It was noticed that the successive curves for any solution could not be exactly superimposed upon one another, but that there was an apparent increase in sensitiveness of the solution with illumination. This was found true even when the solution had not been recently exposed to light.

Such an apparent increase in sensitiveness would occur if the molecules of the solution,—changed in some way by the action of the light,—had not had time to return to their original condition before the next exposure. In several cases this increase was gradual at first and then the sensitiveness jumped to a higher value, after which, the remaining curves were pretty well bunched together (Fig. 10). This scattering effect became less with age, both when the solution had stood "in the light" and when it was "in the dark."

When the first set of curves were taken, the cell was left in the dark only long enough for the photoelectric current to come back to its zero

(dark current) value. This took from about three minutes for short exposures, to five or six minutes for longer ones, with the result that, compared to the length of exposure, the solution was in the dark much longer after short exposures than it was after the longer ones. In taking the later curves, it was made the rule to wait at least four times the length of the preceding exposure, counting from the time the shutter was closed, before illuminating the cell again. Even with this precaution, the sudden increase in sensitiveness sometimes occurred, but, on the whole, the curves tended to be more uniformly distributed.

FIGURE 10



If, for any reason, a considerable length of time, *e.g.*, three fourths hour, elapsed between two consecutive curves, the sensitiveness was found to be somewhat less.

According to Goldmann, there are at least three effects involved in producing such time-current curves:

1. The sensitiveness of the solution to light.

2. Polarization of the dark electrode, which causes a diminution of the current obtained.

3. Something called "fatigue" which causes the loss of sensitiveness with continued illumination. To these might be added whatever causes the tendency to increased sensitiveness during moderately strong illumination.

Goldmann also obtained a curve which passed through a maximum similar to curve 2, Fig. 8, but he obtained it by subjecting a saturated solution to very intense illumination. For less intense light, this same solution gave a curve of the same general shape as curve *E*, Fig. 3. He kept the concentration constant and varied the illumination, whereas I have varied the former and kept the latter constant.

Goldmann explained[1] the passing of the current through such a maximum by saying that after the potential of the illuminated electrode has reached a certain value, the losses, such as:—diffusion of negative

[1] *Loc. cit.*, p. 510.

charges through the solution to the positive electrode, the recombination of positive and negative charges, and anything which causes a spontaneous discharge of the electrode, and which increases in size with the potential of the electrode, have now become so large that they can no longer be neglected and that they cause the falling off of the current.

Until some means is found for eliminating some of these components while the others are studied, it seems rather hopeless to try to estimate the relative value of any one, in the composite curve obtained.

Before any solution was taken from the cell, its electrolytic resistance R_s was measured by the high frequency alternating current and telephone method. The reciprocal of the resistance of the cell filled with alcohol alone, R_a, was subtracted from the reciprocals of the values so obtained and the result divided by the concentration in per cent. This quantity, which is proportional to the per cent. ionization of the solutions, was plotted against the concentration in per cent. The form of the curve (Fig. 11) shows that Rhodamine-B in alcohol is a strong electrolyte.

FIGURE 11

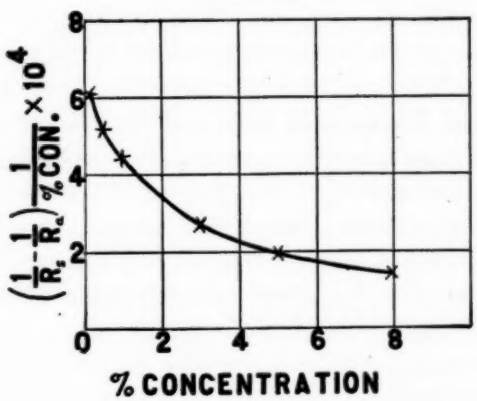


TABLE I.

Concentration in Per Cent. by Weight.	R_s in Ohms.	$1/R_s$	$(1/R_s - 1/R_a)1/$Per Cent. Concentration.
0.000	170,430	0.0574×10^{-4}	
0.224	7,735	1.292 "	6.17×10^{-4}
0.483	3,762	2.658 "	5.19 "
0.980	2,247	4.450 "	4.39 "
2.880	1,224	8.17 "	2.70 "
4.984	994	10.06 "	2.01 "
7.890	863	11.59 "	1.45 "

THE EFFECT OF FLOW OF LIQUID AGAINST ELECTRODES.

A slight variation in the regular procedure was made in an attempt to determine the effect on the photoelectric current when a constant supply of fresh electrolyte was kept moving past the electrodes. For this purpose, the cell was connected to two reservoirs in such a way that the liquid could be forced through it in either direction and at any desired speed.

It was found that, when the liquid was forced through the cell from the upper tank to the lower one, the galvanometer was consistently deflected to the left, whereas, when the direction of flow was reversed, the deflection also reversed. In both cases the magnitude of the deflection was roughly proportional to the rate of flow, although it was always larger when the liquid was drawn up through the cell than when it was forced down. In all cases the deflection lasted only as long as the liquid was in motion. When the flow stopped, the current fell rapidly to zero.

A further study of the liquid currents through the cell in the two cases, led to the conclusion that there was a selective flow of electrolyte against the electrodes in each case, the "in" current flowing more strongly against the one than the "out" current against the other. This might account for the consistent difference in the size of the electrical effects observed.

Apparently, then, a stream of electrolyte against an electrode causes it temporarily to become more negative, irrespective of its previous charge. The negativeness is a function of the force with which the liquid strikes the electrode. The stream has the same effect upon the dark current that substituting a thinner electrode film for the bombarded electrode would have. The effect was the same when superimposed upon a small but steady photoelectric current.

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TEMPERATURE EFFECT IN BARIUM AND STRONTIUM PHOTO-ELECTRIC CELLS.

By Theodore W. Case.

Synopsis.

Photo-electric Current from Treated Barium and Strontium Surfaces.—A metal plate mounted in an evacuated cell was outgassed by heating inductively and was then coated with barium or strontium. The large temperature effect previously reported was confirmed. At dull red heat the current from the two metals was found to be respectively 1,200 and 25 times as great as at room temperature.

IN the Physical Review for March, 1921, in a brief: "New Strontium and Barium Photo-Electric Cells" the author mentioned the fact that the photo-electric current was increased about 100 times when the metal plate upon which the metallic barium was deposited was raised in temperature to just under a red heat. This was accomplished by passing a current through the metallic plate, but previously to coating with the active material the plate had not been entirely freed of gases, with the result that the barium was oxidized and the action spoiled, but not before the one hundred time increase had been observed. The resulting contamination and gas present made it doubtful as to whether the observed increase was due to a true temperature effect or not. Since then Merritt has also observed this effect on the oxide-coated filaments of audion bulbs.[1]

Recently the construction of these cells has been refined and extremely careful precautions taken in freeing all the metallic parts of gas by raising them to a bright red heat until all traces of gas have disappeared. This has been accomplished by the induction furnace method which is ideal for this work. The metal plate is then coated with either barium or strontium as desired. It is now very simple to observe the temperature effect on the photo-electric current by inductively heating the plate from the outside of the vacuum bottle, and the cell does not spoil unless the plate is heated to such a bright red that the material is actually volatilized off the plate, in which case most of it goes over and is deposited on the opposite electrode. This occurs, however, only when the plate has been heated to a bright red.

With these arrangements the author has checked his previous finding of a large temperature effect in the case of barium and a much smaller

[1] Ernest A. Merritt, Photoelectric Phenomena in Coated Filament Audion Bulbs, Phys. Rev., April, 1921.

one in the case of the strontium. For strontium, the increase is only about 25 times at a dull red heat. The action is not spoiled as it previously was, because no gas is given off the plates. When these cells are giving their maximum photo-electric current under high temperature, there is not over .4 per cent. thermo-electric current if the light be turned off the cells.

The increase of photo-electric current is gradual with increase or decrease in temperature, as illustrated by observing the galvanometer deflection slowly decrease as the plate cools from a red heat. There are no sudden jumps in the photo-electric current curve, although it is impossible at present to tell whether the increase is directly proportional to the temperature or not until a cell has been constructed with a thermo junction on the plate so as to get an accurate temperature curve.

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